

I

HIGH-TEMPERATURE CORROSION IN GAS TURBINES AND STEAM BOILERS BY FUEL IMPURITIES.
PART VIII. EVALUATION OF THE EFFECTS OF MANGANESE, CALCIUM, AND SEVERAL HEAVY
METALS ON CORROSION AND SLAG FORMATION

Walter R. May, Michael J. Zetlmeisl, Robert R. Annand, David F. Laurence

TRETOLITE DIVISION/PETROLITE CORPORATION, 369 Marshall Avenue, St. Louis, MO. 63119

INTRODUCTION

There are two recognized approaches to controlling vanadic corrosion. Both result in the production of dry, non-adhering and therefore non-corroding slags. The more widely accepted approach is the formation of higher melting compounds in the slag via fuel additives. The other approach utilizes low excess air operating conditions which produce higher melting, lower valence state vanadium compounds and less SO_3 which reduces sulfate in the slag. In earlier studies presented in this series of papers¹, we have examined magnesium, silicon, aluminum, and combinations of these elements as additives. Many elements have been tried as additives with varying degrees of success²⁻⁶. The difficulty in obtaining sufficient data to thoroughly evaluate an additive partially explains the paucity of information on combination systems. Our electrochemical approach to measuring corrosion rates coupled with the stepwise linear regression analysis of the data helps fill this gap and offers a rapid but thorough screening of an additive system. The technology in this area, particularly for gas turbines, has been toward use of lower quality fuels and higher temperatures for better efficiency. The result has been a demand for an additive with better sodium and temperature tolerances. In the last paper in this series¹, we presented data on the magnesium-aluminum-silicon system which showed considerable promise in this area. In this paper, we are presenting data obtained on several other systems of interest.

Manganese improves combustion efficiency which permits lower excess air operation¹⁰. Available commercially are combinations with magnesium and/or silicon to permit low excess air operation where possible with the magnesium and/or silicon present to inhibit slagging and corrosion in the conventional manner. The purpose of the study on manganese was to find if it has any inhibiting effects in the conventional manner or interferes with magnesium and/or silicon. The purpose of studying calcium, zirconium and the rare earths was to evaluate their effects on the corrosion process and slag characteristics.

EXPERIMENTAL

Materials. The melts were prepared from reagent grade chemicals obtained from Fisher Scientific Company with the exception of the following. The cerium oxide, zirconium oxide and rare earth oxide mixture were obtained from the Davison Chemical Division of W.R. Grace and Company. The rare earth oxide mixture contained approximately 48% CeO_2 , 23% La_2O_3 , 5% Pr_6O_{11} , 16% Nd_2O_3 , 4% Sm_2O_3 and 4% of other rare earth oxides. Samples of 40 g size were prepared by weighing appropriate quantities of the constituents and thoroughly mixing to insure a homogeneous sample.

The fuel for the burner test was reagent grade hexanes and xylenes. Vanadium was added in the form of an oil-soluble material, vanadium Ten-CemTM (6 percent vanadium), obtained from Mooney Chemicals, Inc. The sodium was added as an oil-soluble sodium-naphthenate prepared in this laboratory by neutralizing an industrial grade naphthenic acid with sodium hydroxide. The final product contained 4.3 percent sodium as determined by atomic adsorption. The magnesium was added as KONTOLTM KI-15 containing 10 percent metal. The silica was added as KONTOLTM KI-39d, containing 16 percent metal. The magnesium-silicon mixture was KONTOLTM KI-18d containing 8 percent of each metal. These are oil-soluble compounds from the TRETOLITE DIVISION of PETROLITE CORPORATION. The aluminum source was a sulfonate obtained from Witco Chemicals Company containing 14.4 percent metal. Sulfur was added as a substituted 1, 2-dithio, 3-thione (36 percent sulfur)

prepared in the TRETOLITE DIVISION's pilot plant.

Electrochemical Measurements. The corrosion rate measurements were made in an electrochemical cell consisting of three electrodes immersed in a slag of the desired composition. The corrosion current was determined from polarization curves or by the polarization admittance technique. The cell, corrosion rate measuring apparatus, source of materials, and sample preparation techniques are described in our earlier paper⁷.

Slag Test. The slag test consisted of burning a fuel containing the desired levels of contaminants and inhibitors. The flame impinges upon a coupon which is adjusted to give the desired temperature. The slag characteristics are evaluated by measuring the amount of material that can be brushed from the coupon. The test is described in much greater detail in an earlier publication⁸.

RESULTS

Corrosion rate data from $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5\text{-MnO}_2$ systems containing various combinations of magnesium and silicon are presented in Table I - III. The correlation equations generated by the technique described earlier⁹ are presented in Table V. Comparisons of corrosion rates found in these slags with other additive systems at 800° and 900° are given in Figure 1 and 2. Data for the $\text{Na}_2\text{SO}_4\text{-CaSO}_4\text{-V}_2\text{O}_5$ system are given in Table IV. The correlation equations for this system and those containing aluminum, silicon and lead are given in Table V. Also included in Table V are equations for the systems containing ZrO_2 , CeO_2 and ReO_2 the rare earth oxide combination. The data for these are not included to maintain a reasonable size for this paper. However, these data are available on request from the authors. The correlation equations for the MgSO_4 and $\text{MgSO}_4\text{-SiO}_2$ systems are included for comparison with the data presented in this paper. The plots for these two are also found in Figure 1 and 2. In all cases, the Na/V coefficients are positive indicating the strong corrosion promoting effect of sodium. The coefficient for Mn/V is positive indicating that manganese promotes corrosion. We examined several other cases where the Mn/V + Pb ratio was held at 2. In those cases, the Mg (+Si)/V (+Pb) ratios were negative indicating that the additive inhibited corrosion. We chose those cases because in actual practice, the manganese level is more likely to be held constant while the Mg + Si level varies with the trace metal content in the fuel.

Another interesting observation was that although calcium was an inhibitor when present alone, it promoted corrosion in relation to aluminum and silicon when all were included. Although the rare earths had negative coefficients, corrosion currents predicted by the correlation equations indicated that these materials were not inhibitors. All coefficients are included in the correlation equations although they are not always statistically significant. In those cases in which the F level was below approximately 2.25, there is less than a 95% chance that all the coefficients are significant for the correlation. However, addition of these does not materially effect the standard error and it is worthwhile to include these in our examination of their effect on the corrosion rate.

Slag friability data for the calcium-aluminum-silicon system compared with magnesium and magnesium-silicon are presented in Table VI. The data for various Na/V levels are summarized for comparison. There were not enough data to evaluate with the linear stepwise regression analysis technique. However, the effect of sodium, additive and temperature are clearly evident. At 820°, the Ca-Al-Si system compares favorably with the Mg-Si system. However, at 900° and particularly the high Na/V ratios, the friability decreases very rapidly.

DISCUSSION

Over the past several years, the trade literature has abounded with claims for the effects of manganese on fireside corrosion, slag problems and cold-end corrosion¹⁰. There now appears little doubt that manganese as well as a few other metals such as iron and copper will reduce carbonaceous effluents or smoke through

more efficient combustion processes¹¹. This type of additive is known as a combustion improver.

The minimum level of excess air required to eliminate smoke is a function of the engineering of the piece of equipment. Smoking can occur even in a gas turbine in spite of an overall oxygen/fuel ratio of 15 passing through the machine. The problem is caused by burner tip malfunctions and lack of available oxygen in the burner cans. Excess air is used to a lesser extent in other types of combustion equipment such as boilers to prevent smoking. During combustion of low quality fuels under excess air conditions, pentavalent vanadium compounds such as V_2O_5 and NaV_2O_6 with low melting points occur. Moreover, there is an increased production of SO_3 which leads to formation of Na_2SO_4 in slags and H_2SO_4 downstream. A combustion improver allows operation near the stoichiometric ratio of air to fuel eliminating the problem delineated above. Furthermore, lower excess air operation yields considerable fuel savings due to more efficient operation of the burner.

Use of a combustion improver does require careful application by the operator. If the equipment does not permit good control of excess air, the air/fuel ratio, protection will not be attained in this manner. A combination additive has many benefits for equipment with poor control of air/fuel ratio. The manganese yields all the advantages of low excess air operation while magnesium and/or silicon gives protection during periods of excess air operation. A question we have tried to answer here is: Does manganese interfere with the corrosion inhibiting effects of magnesium and silicon?

The data in Table I reveals that manganese is not an inhibitor and appears to promote corrosion. We feel that this effect is due to addition of liquids to the melt by the manganese. The effect of manganese on the inhibiting effect of magnesium and magnesium-silicon are shown in Table II and III and Figure 1 and 2. Manganese detracts from the inhibiting effect of magnesium and silicon, although satisfactory protection can be attained at 800° with the Mg-Si combination. Comparison of the Mn-Mg and Mn-Mg-Si curves with the Mg and Mg-Si curves in Figures 1 and 2 illustrate this point.

We know of no published work to corroborate these findings and would welcome experiments of this nature. However, the laboratory data presented here leads us to conclude that manganese in combination with magnesium and magnesium-silicon can be beneficial at lower temperature. At higher temperatures, manganese apparently contributes to the liquidus phase of the slag and can be detrimental to Mg and Mg-Si. In either case, the operator should apply Mn-Mg and Mn-Mg-Si combinations with a great deal of care and with full knowledge of the protection mechanism for this type of additive.

Calcium has been cited as a problem contaminant in fuels for gas turbines and boilers². We evaluated calcium and several combinations with aluminum, silicon and lead. The conclusion is that calcium is a corrosion inhibitor and in the presence of aluminum and silicon exhibits a tolerance to sodium at 900° which is similar to that found for the Mg-Al-Si combination. However, a study of the slag data presented in Table VI indicates that calcium produces unacceptable slags, particularly at the higher temperatures and sodium levels. The adverse slagging behavior cancels benefits from corrosion protection. These results are consistent with private communications we have received from equipment manufacturers.

In our search for better vanadic corrosion inhibitors, we have evaluated several heavy elements. Data on zirconium, cerium and the rare earth mixture described above are presented in Table V. All of these systems exhibit corrosion rates similar to those for manganese and do not inhibit corrosion.

CONCLUSIONS

1. Manganese contributes to corrosion in Na_2SO_4 - V_2O_5 melts and will not inhibit corrosion by forming higher melting compounds.
2. Manganese interferes with the corrosion inhibiting effects of magnesium and silicon.

3. Combinations of manganese, magnesium and silicon are probably safe at 800°C (1473°F) or lower but not at higher temperatures such as 850° or 950°. The Mn-Mg-Si system is preferable to the Mn-Mg system.

4. Calcium inhibits Na_2SO_4 - V_2O_5 corrosion and the calcium-aluminum-silicon combination has good sodium tolerance.

5. Calcium systems form tenacious slags that detract from their corrosion inhibiting effectiveness.

Measurements on the rare earth oxide mixture, on zirconium, and on cerium did not indicate any corrosion inhibiting properties for these systems.

REFERENCES

1. May, W.R., Zetlmeisl, M.J., Annand, R.R., ASME Paper No. 75/WA/CD-6 and earlier papers in this series cited therein.
2. Buchanan, B.O., Gardiner, C.R., Sanders, G.G., ASME Paper No. A-52-161.
3. Lee, S.Y., Young, W.E., Vermes, G.I., ASME Paper No. 73-GT-1.
4. Lee, G.K., Mitchell, E.R., Grimsey, R.G., Hopkins, S.E., Proceedings of the American Power Conference, 26, 531, 1964.
5. Lee, G.K., Fuel Society Journal, 20, 8, (1969).
6. Lee, S.Y., Young, W.E., ASME Paper No. 75-WA/CD-1.
7. May, W.R., Zetlmeisl, M.J., Bsharah, L., Annand, R.R.
I & EC Product Research and Development, 11, 438 (1972).
8. May, W.R., Zetlmeisl, M.J., Bsharah, L., J. Eng. Power, Trans., ASME, Series A., 96, 124, (1974).
9. May, W.R., Zetlmeisl, M.J., Annand, R.R., ASME Paper No. 75-WA/CD-5.
10. Plonsker, L., Rifken, E.B., Geuckstein, M.E., Baile, S.D., Presented at the Central States Section, The Combustion Institute, Madison, Wisconsin, Manual 26-27, 1974.
11. Salooja, K.C., J. Inst. Fuel, 1972, 37.

TABLE 1

CORROSION RATES OF $\text{Na}_2\text{SO}_4 - \text{MnO}_2 - \text{V}_2\text{O}_5$ SLAGS

| WEIGHT RATIOS | | CORROSION CURRENTS (Ma/Cm^2) | | | | | |
|----------------------|----------------------|--|-------|-------|-------|-------|-------|
| Na/V | Mn/V | 700° | 750° | 800° | 850° | 900° | 950° |
| 1 | 1 | .0832 | .1830 | .3171 | .8423 | 1.148 | 1.231 |
| 1 | 2 | 6.83 | 10.25 | 12.30 | 13.21 | 12.52 | 13.43 |
| 1 | 3 | 10.62 | 13.31 | 15.87 | 17.92 | 19.97 | 25.34 |
| 1 | 4 | 9.20 | 11.96 | 14.73 | 19.10 | 20.13 | 23.01 |
| 1 | 5 | 10.65 | 14.20 | 32.67 | 35.51 | 41.19 | 42.61 |
| .1 | 1 | 7.63 | 8.51 | 10.39 | 13.26 | 17.91 | 23.87 |
| .1 | 2 | 1.33 | 1.74 | 2.22 | 2.54 | 2.78 | 3.33 |
| .1 | 3 | .578 | .650 | .795 | 1.04 | 1.56 | 1.99 |
| .1 | 4 | 10.69 | 10.36 | 10.16 | 12.03 | 15.37 | 16.04 |
| .1 | 5 | 3.21 | 4.49 | 6.89 | 11.54 | 14.43 | 12.83 |
| .01 | 1 | 6.21 | 18.63 | 27.94 | 27.94 | 27.94 | 31.04 |
| .01 | 2 | .742 | 1.15 | 1.35 | 1.64 | 2.18 | 2.52 |
| .01 | 3 | 13.65 | 17.07 | 20.48 | 23.55 | 27.31 | 35.16 |
| .01 | 4 | 1.21 | 1.60 | 1.46 | 1.75 | 3.54 | 4.51 |
| .01 | 5 | 1.26 | .762 | .949 | 1.40 | 1.79 | 2.26 |

TABLE II

CORROSION RATES OF $\text{Na}_2\text{SO}_4 - \text{MnO}_2 - \text{MgSO}_4 - \text{V}_2\text{O}_5$ SLAGS

| WEIGHT RATIOS | | | CORROSION CURRENTS (Ma/Cm^2) | | | | | |
|----------------------|----------------------|----------------------|--|-------|-------|-------|-------|------|
| Na/V | Mn/V | Mg/V | 700° | 750° | 800° | 850° | 900° | 950° |
| 1 | 1 | 1 | 1.29 | 1.43 | .644 | .644 | 1.13 | 1.22 |
| 1 | 2 | 2 | .284 | .613 | .643 | .747 | .852 | .942 |
| 1 | 3 | 3 | 1.17 | 1.79 | 1.79 | 2.48 | 2.48 | 2.76 |
| 1 | 4 | 4 | .016 | .040 | .051 | .800 | 1.634 | 1.96 |
| 1 | 5 | 5 | .017 | .030 | .642 | .984 | 1.436 | 1.64 |
| .1 | 1 | 1 | .031 | .053 | .411 | .455 | .632 | 2.13 |
| .1 | 2 | 2 | .0188 | .0286 | .134 | .406 | .436 | 1.16 |
| .1 | 3 | 3 | .0015 | .0031 | .0031 | .100 | .137 | .216 |
| .1 | 4 | 4 | .0015 | .0015 | .019 | .026 | .034 | .059 |
| .1 | 5 | 5 | .0015 | .0045 | .019 | .029 | .035 | .106 |
| .01 | 1 | 1 | .124 | .350 | .617 | 1.07 | 1.52 | 3.77 |
| .01 | 2 | 2 | .059 | .096 | 1.11 | 1.32 | 2.18 | 1.65 |
| .01 | 3 | 3 | 0 | 0 | .0055 | .0055 | .011 | .022 |
| .01 | 4 | 4 | .005 | .011 | .025 | .028 | .029 | .029 |
| .01 | 5 | 5 | .122 | .183 | .305 | .427 | .589 | .792 |

TABLE III

CORROSION RATES OF $\text{Na}_2\text{SO}_4 - \text{MnO}_2 - \text{MgSO}_4 - \text{SiO}_2 - \text{V}_2\text{O}_5$ SLAGS

| WEIGHT RATIOS | | | | CORROSION CURRENTS (Ma/Cm^2) | | | | | |
|----------------------|----------------------|----------------------|----------------------|--|-------|-------|-------|--------|-------|
| Na/V | Mn/V | Mg/V | Si/V | 700° | 750° | 800° | 850° | 900° | 950° |
| 1 | 2 | 1 | 1 | .09785 | .2039 | .2854 | .4077 | .5912 | .8766 |
| 1 | 2 | 2 | 2 | .0245 | .1116 | .2232 | .3794 | .4909 | .6472 |
| 1 | 2 | 3 | 3 | .0033 | .0083 | .2499 | .3500 | .4833 | .6333 |
| 1 | 2 | 4 | 4 | .0017 | .0033 | .1081 | .1829 | .3326 | .4823 |
| 1 | 2 | 5 | 5 | .0011 | .0031 | .0105 | .1600 | .2526 | .4632 |
| .1 | 2 | 1 | 1 | .0037 | .0075 | .0125 | .0131 | .0225 | .0299 |
| .1 | 2 | 2 | 2 | .0008 | .0008 | .0015 | .0015 | .00225 | .0090 |
| .1 | 2 | 3 | 3 | .0009 | .0013 | .0019 | .0019 | .0019 | .0085 |
| .1 | 2 | 4 | 4 | .0009 | .0009 | .0009 | .0010 | .0019 | .0058 |
| .1 | 2 | 5 | 5 | .0023 | .0023 | .0034 | .0046 | .0068 | .0091 |
| .01 | 2 | 1 | 1 | .0023 | .0023 | .0045 | .0124 | .0360 | .0450 |
| .01 | 2 | 2 | 2 | .0011 | .0044 | .0111 | .0313 | .0469 | .0603 |
| .01 | 2 | 3 | 3 | .0011 | .0018 | .0022 | .0022 | .0022 | .0054 |
| .01 | 2 | 4 | 4 | .0023 | .0023 | .0034 | .0034 | .0045 | .0068 |
| .01 | 2 | 5 | 5 | .0016 | .0016 | .0016 | .0016 | .0062 | .0094 |

TABLE IV

CORROSION RATES OF $\text{Na}_2\text{SO}_4 - \text{CaSO}_4 - \text{V}_2\text{O}_5$ SLAGS

| WEIGHT RATIO | | CORROSION CURRENTS (Ma/Cm^2) | | | |
|----------------------|----------------------|--|-------|------|------|
| Na/V | Ca/V | 800° | 850° | 900° | 950° |
| 1 | 1 | 65 | 108 | 81.2 | 54.2 |
| 1 | 2 | 17.1 | 34.1 | 47.8 | 54.5 |
| 1 | 3 | 18.7 | 33.4 | 28.0 | 32.7 |
| 1 | 4 | 3.73 | 6.35 | 9.69 | 11.2 |
| 1 | 5 | 6.59 | 7.33 | 14.6 | 32.3 |
| .1 | 1 | 7.54 | 11.9 | 13.7 | 13.0 |
| .1 | 2 | 3.31 | 4.26 | 4.72 | 5.67 |
| .1 | 3 | 1.18 | 1.38 | 1.54 | 1.63 |
| .1 | 4 | .888 | 1.05 | 1.37 | 1.69 |
| .1 | 5 | .994 | 1.19 | 1.49 | 1.49 |
| .01 | 1 | 19.9 | 24.4 | 28.1 | 23.7 |
| .01 | 2 | 3.12 | 3.12 | 3.45 | 3.45 |
| .01 | 3 | 2.43 | 3.21 | 4.86 | 6.61 |
| .01 | 4 | .044 | .072 | .092 | .100 |
| .01 | 5 | .143 | .428 | .443 | .457 |
| .001 | 1 | 6.04 | 9.06 | 9.66 | 9.66 |
| .001 | 2 | 2.01 | 2.29 | 2.73 | 3.01 |
| .001 | 3 | .290 | .347 | .463 | .578 |
| .001 | 4 | .0966 | .0966 | .104 | .112 |
| .001 | 5 | .214 | .268 | .322 | .375 |

TABLE V

Correlation coefficients for the corrosion rate data

$$I_{corr} = A + B (Na/V) + C (Mg/V) + D (Mn/V) + E (Mo/V) + G (\text{Temp} \cdot C)$$

| System | Correlation Equations | | | | | | N Sets Data | F Level | No/V Range | | Add/V Range | | Temp. Range | |
|--|-----------------------|-------|--------|--------|---------|--------|-------------|---------|------------|------|-------------|------|------------------|------------------|
| | A | B | C | D | E | G | | | Low | High | Low | High | Low | High |
| $Na_2SO_4-MgSO_4-V_2O_5$ | -12.83 | 11.41 | - | -1.894 | - | 0.0212 | 60 | 3.11 | 0.01 | 1.0 | 1.0 | 1.0 | 1.0 | |
| $Na_2SO_4-MgSO_4-SiO_2-V_2O_5$ | -11.66 | 19.61 | - | -1.886 | -0.6678 | 0.0187 | 137 | 0.89 | 0.001 | 1.0 | 2.0 | 6.0 | 700 ^c | 950 ^c |
| $Na_2SO_4-MnO_2-V_2O_5$ | -27.4 | 6.14 | 0.677 | - | 0.0414 | 0.0414 | 90 | 0.89 | 0.01 | 1.0 | 1.0 | 5.0 | 700 ^c | 950 ^c |
| $Na_2SO_4-MnO_2-MgSO_4-V_2O_5, Mn/V = Mo/V$ | -2.30 | 0.743 | -0.184 | - | - | 0.0038 | 90 | 17.0 | 0.01 | 1.0 | 1.0 | 5.0 | 700 ^c | 950 ^c |
| $Na_2SO_4-MnO_2-MgSO_4-SiO_2-V_2O_5, Mg/V=Si/V, Mn/V=Z$ | -0.630 | 0.274 | -0.024 | - | - | 0.0068 | 90 | 8.32 | 0.01 | 1.0 | 1.0 | 5.0 | 700 ^c | 950 ^c |
| $Na_2SO_4-MnO_2-MgSO_4-PbO-V_2O_5, Mg/Pb+V=Z, Pb=V, Mn/V=Z$ | -2.41 | 0.970 | -0.232 | - | - | 0.0039 | 90 | 28.9 | 0.01 | 1.0 | 1.0 | 5.0 | 700 ^c | 950 ^c |
| $Na_2SO_4-MnO_2-MgSO_4-SiO_2-PbO-V_2O_5, Mn/Pb+V=Z, Pb=V, Mg=Si$ | -1.28 | 0.573 | 0.018 | - | - | 0.0016 | 90 | 0.89 | 0.01 | 1.0 | 1.0 | 5.0 | 700 ^c | 950 ^c |
| $Na_2SO_4-CeSO_4-V_2O_5$ | -3.89 | 29.9 | -6.19 | - | Si/V | 0.0273 | 80 | 1.49 | 0.001 | 1.0 | 1.0 | 5.0 | 800 ^c | 950 ^c |
| $Na_2SO_4-CeSO_4-Al_2O_3-V_2O_5$ | -14.2 | 9.00 | -1.76 | -3.13 | - | 0.0262 | 106 | 3.16 | 0.01 | 1.0 | 1.0 | 5.0 | 800 ^c | 950 ^c |
| $Na_2SO_4-CeSO_4-SiO_2-V_2O_5$ | -9.65 | 7.15 | -1.31 | - | -2.11 | 0.0202 | 127 | 9.53 | 0.001 | 1.0 | 1.0 | 5.0 | 800 ^c | 950 ^c |
| $Na_2SO_4-CeSO_4-Al_2O_3-SiO_2-V_2O_5$ | -2.75 | 2.25 | 0.300 | -1.08 | -1.39 | 0.0068 | 96 | 0.71 | 0.01 | 1.0 | 3.0 | 6.0 | 800 ^c | 950 ^c |
| $Na_2SO_4-CeSO_4-Al_2O_3-PbO$ | -9.24 | 0.151 | 0.0081 | - | - | 0.0114 | 48 | 0.003 | 0.01 | 1.0 | 1.0 | 5.0 | 800 ^c | 950 ^c |
| $Na_2SO_4-CeSO_4-Al_2O_3-PbSO_4$ | -1.65 | 0.007 | -0.117 | -0.117 | - | 0.0026 | 44 | 0.294 | 0.01 | 1.0 | 1.0 | 5.0 | 800 ^c | 950 ^c |
| $Na_2SO_4-ZrO-V_2O_5$ | -13.9 | 3.70 | -187 | - | - | 0.0190 | 64 | 0.670 | 0.001 | 1.0 | 1.0 | 5.0 | 800 ^c | 950 ^c |
| $Na_2SO_4-CeO-V_2O_5$ | -5.66 | 6.85 | -1.67 | - | - | 0.0136 | 80 | 4.31 | 0.001 | 1.0 | 1.0 | 5.0 | 800 ^c | 950 ^c |
| $Na_2SO_4-ReO_3-V_2O_5$ | -5.32 | 2.39 | -5.62 | - | - | 0.0314 | 76 | 1.20 | 0.001 | 1.0 | 1.0 | 5.0 | 800 ^c | 950 ^c |

TABLE VI

Comparison of slag Test Data From the Calcium-Aluminum System
With Data From the Magnesium-Silicon System

| System | Average % Loss on Brushing | |
|-----------------------------------|----------------------------|------|
| | 820° | 900° |
| Na/V = 0 | | |
| Mg/V = 3 | 1.9 | 10 |
| Mg/V = 6 | 11.7 | 20 |
| Mg/V = Si/V = 3 | 58 | 59 |
| Ca/V = .75, Al/V = 2.25, Si/V = 3 | 63 | 26 |
| Na/V = .01 | | |
| Mg/V = 3 | 2.7 | 8.33 |
| Mg/V = 6 | 35 | 14 |
| Mg/V = Si/V = 3 | 53 | 6.3 |
| Ca/V = .75, Al/V = 2.25, Si/V = 3 | 59 | 8.41 |
| Na/V = .1 | | |
| Mg/V = 3 | 2.1 | 0 |
| Mg/V = 6 | 22 | 13.2 |
| Mg/V = Si/V = 3 | 35 | 18 |
| Ca/V = .75, Al/V = 2.25, Si/V = 3 | 61 | 7.7 |
| Na/V = 1 | | |
| Mg/V = 3 | 1.5 | 0 |
| Mg/V = 6 | 4 | 3.3 |
| Mg/V = Si/V = 3 | 11.2 | 15.3 |
| Ca/V = .75, Al/V = 2.25, Si/V = 3 | 1.3 | 1.4 |

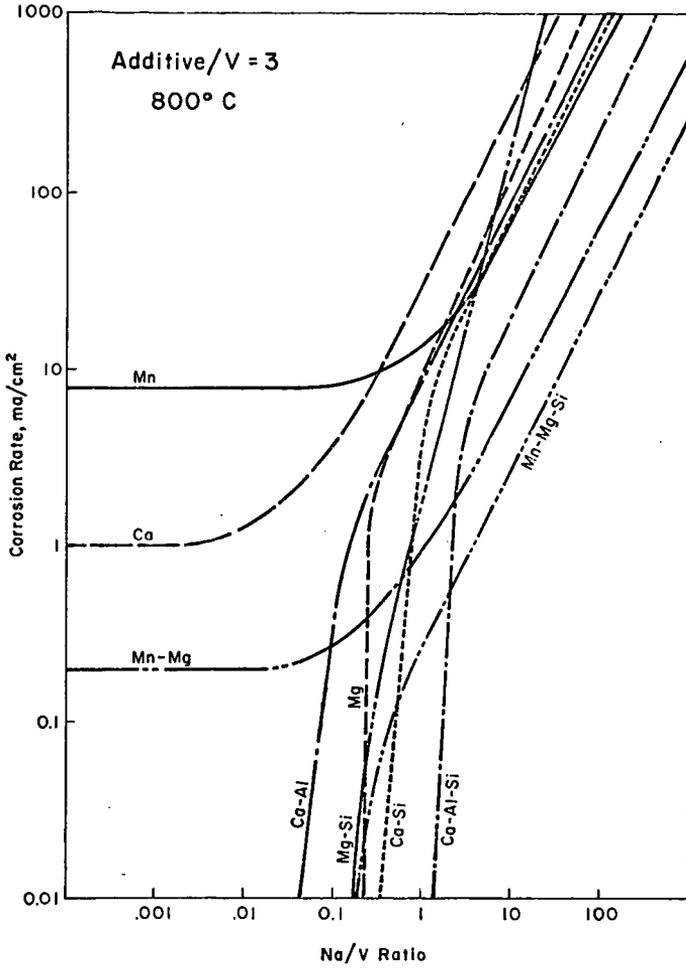


FIGURE 1 - Corrosion Rates vs. Na/V Ratios for Several Additives at 800°C

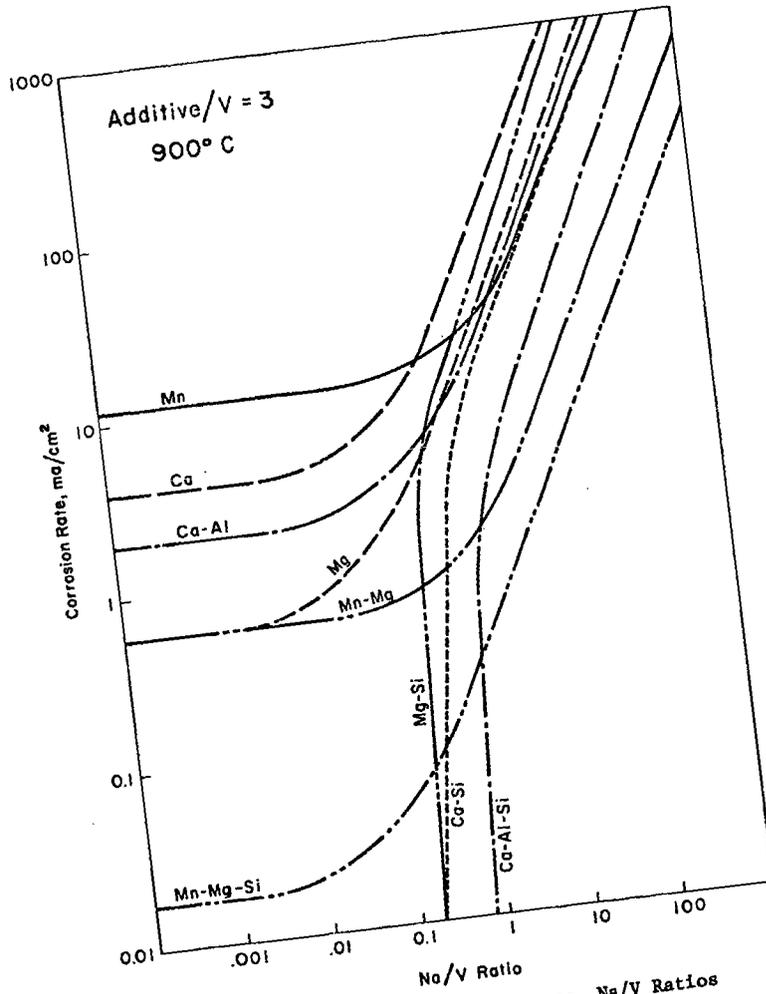


FIGURE 2 - Corrosion Rates vs. Na/V Ratios
 for Several Additives at 900°C

OIL ASH CHEMISTRY IN UTILITY BOILERS AS RELATED TO ADDITIVE TREATMENT.

J. T. Mitchell, Martin Marietta Chemicals, Refractories Division,
1450 South Rolling Road, Baltimore, Maryland 21227.

Several hundred sets of ash samples from boilers of varied design, burning heavy oils have been analyzed by means of wet chemistry, XRF, XRD, SEM, and petrographic analyses. Other tests were performed to determine solubilities and melting behaviors. Most oil ashes can be characterized on the basis of four components: V_2O_5 , Na_2O , MgO (or XO), and SO_3 which control the chemical and physical properties of deposits formed. Oils are categorized into three major groups on the basis of quantities of S, V, and Na and on the ratio Na/V. These categories are: (1) high V and S, low Na, (2) medium V and S, low to medium Na, and (3) low V and S, medium to high Na. Variations in ash chemistry are related to additive rates, to amounts and ratios of oil impurities, and to relative location in the boiler where the ash was deposited. Physical properties of ash deposits are dependent on the position in the boiler, on the types and quantities of phases present, and on the distribution of these phases within the deposits.

USE OF THE DEW POINT METER AND ASH SAMPLER IN ASSESSING
PERFORMANCE OF FUEL OIL ADDITIVES

by

J. E. Radway, Assistant
Vice President, Technology

and

M. W. DiCarlo, Product
Manager, Power Chemicals

BASIC CHEMICALS
Cleveland, Ohio

INTRODUCTION

Many severe problems are associated with sulfuric acid corrosion caused by conversion of a portion of sulfur in heavy fuel oils to sulfur trioxide by the combustion process in steam boilers. In order to evaluate various practical means of minimizing the problem at the plant level, meaningful but relatively easy tests had to be developed. This paper shows that acid dew point measurements of the flue gases before and after the air preheater are fairly predictive of the acid condensation occurring and its corrosion potential. Use of fuel oil additives can complicate the data collection and interpretation, necessitating supplemental techniques to gauge the neutralization which can take place, both in the gas stream and on the heat exchange surfaces. One such supplemental technique, based on ash collected from the gas stream after the air preheater, is described and a case history presented to show its application in evaluating additives in a modern power station where more sophisticated techniques cannot be readily applied. Results of these techniques quickly show if an additive is effective in controlling sulfuric acid corrosion.

EXPERIMENTAL

The boiler used for the experimental work is a 600-Mw Combustion Engineering utility boiler designed to burn residual fuel oil and equipped with two regenerative type air preheaters. The fuel oil throughout the test period consisted of a typical Venezuelan residual oil containing 0.1 percent ash, an average of 2 percent sulfur and 350 to 500 ppm vanadium.

All measurements and samples included correlation of the boiler operating data which are known to directly affect the amount of sulfur trioxide formed and resulting acid condensation. These data are: rate of firing (load), excess air, and average metal temperature of the heat exchange elements in the air preheaters. Fuel oil flow varies directly with load and is typically half pound per hour per kw of load.

Measurements were taken at various firing rates and with two chemical treatments. One treatment was supplied as fuel oil additive and the other as a "cold end" treatment by injection of chemicals into the hot gases ahead of the air preheaters.

To reduce the total experimental time, two cold end treatments were run simultaneously by treating each air preheater separately. Testing was done with no chemical treatment and also with the following single or combination of treatments:

1. Injection into the fuel oil of a commercial fuel oil additive consisting of a dispersion of an inorganic manganese compound.
2. Injection of a commercial fuel oil additive consisting of a combination magnesium/aluminum in a ratio of 10:1 Mg/Al as magnesium oxide and aluminum hydroxide.
3. Injection of the manganese fuel oil additive with concurrent treatment of the air preheaters. One air preheater with a proprietary aqueous magnesium hydroxide slurry and the other with a proprietary powdered additive.
4. The magnesium/alumina combination fuel oil additive with the cold end treatments.

Dew point measurements were taken both before and after the air preheaters with a Land Instruments Inc., Model 200 Dew Point Meter. This instrument was also used to determine the rate of acid condensation (rate of acid build-up or RBU) at various temperatures by controlled cooling with air of the sensor probe inserted into the gas stream.

The dew point meter has been employed for many years in investigations of the corrosion and fouling of low-temperature heat transfer surfaces on both coal and oil-fired boilers. In a 1963 ASME paper, Clark and Childs described its use in developing a "guide" for air heater temperature control.* They showed the importance of low excess air operation, boiler cleanliness and magnesia additives on flue gas corrosion potential. Operation of the dew point meter has been described in previously published material.

Ash sampling was accomplished by collecting a "grab sample" of particulate from the gas stream by insertion of a proprietary aspirator type sampler (Figure 1) into the gas stream after the air preheater.

The ash sample was ground and a one-gram sample was stirred into sufficient distilled water to make a 1 percent slurry. The pH of this slurry was measured one minute after agitation was stopped using a conventional pH meter.

RESULTS AND DISCUSSION

Operational history of this unit indicated a continuing degradation of "cold end" conditions resulting in increased sulfuric acid condensation. These conditions caused accelerated corrosion and fouling of the air preheater, necessitating washing every six weeks.

* N. D. Childs, G. D. Clark, "Boiler Flue Gas Measurements Using a Dew Point Meter" -- ASME 63-WA-109, November, 1963.

This fouling of air preheaters is a typical result of condensed sulfuric acid permitting wet air preheater elements to act as a trap for fly ash.

Design factors in the heat exchange surface of the unit encouraged plant operators to select a manganese type fuel oil additive. Dew points with the manganese fuel oil additive averaged 285°F. (141°C.) and the rate of acid condensation (hereafter referred to as rate of acid build-up -- RBU) measured 1,200 to 1,500 microamps per minute. (Figure 2, 12-6-74) Clark and Childs reported that they found very rapid corrosion on boilers showing an RBU in excess of 500 microamps per minute and relatively minimal problems when this reading was below 100.

The significance of these dew point measurements can be seen by analyzing the data in the first entry on Table I. The pH of fly ash samples measured 1.4 and confirms the high acid dew point and RBU values. It is evident that the manganese fuel oil additive was doing very little to ameliorate severe acidic conditions.

This dew point and pH data in conjunction with the fouling frequency of the air preheater and the marked corrosion noted during visual inspections convinced station personnel that additional steps had to be taken to protect the cold end. They chose to evaluate two proprietary cold end treatments -- an aqueous magnesium hydroxide slurry and an alkaline dry powder product. Each of these were introduced upstream of the air preheater into a zone where flue gas temperatures range from 600-700°F. (316-371°C.)

These chemical treatments lowered the acid dew point to 260°F. (127°C.) and 270°F. (132°C.) respectively and the peak acid condensation temperatures to 220°F. (104°C.) and 240°F. (116°C.) respectively. The RBU values also were lowered to 120 and 110 microamps per minute (Figures 2 and 3). Little acid will condense and little corrosion will occur even though the exit gas temperatures are below the acid dew point. Raising the exit gas temperature to about 279°F. (137°C.) would have the same effect on the RBU value as the alkali, but at a considerable cost in fuel dollars. At 279°F. (137°C.), the rate of acid condensation would be the same as it is with alkali at the present exit gas temperature of 245°F. (118°C.), i.e., 68 microamps per minute.

This data indicates the aqueous magnesium hydroxide slurry to be more effective than the dry powdered product when compared on an equivalent weight basis. Both products depressed the dew point and RBU readings but not to the same degree (Figure 4).

Fireside conditions, after prolonged use of the manganese fuel oil additive, convinced the operators to replace it with the magnesium/aluminum front end treatment. Data with this treatment and no cold end additive show that the dew point was unchanged at both high and low load operations, i.e., 285°F. (141°C.). However, the potential for cold end corrosion did improve as indicated by the rate of acid condensation and ash pH data. The RBU values at high and low loads were in the ranges of 500 and 120 microamps per minute and the corresponding ash pH readings were about 3.0 and 2.5 respectively. These compare with much higher peak rates of condensation (approximately 1,500 microamps per minute) and lower pH values (approximately 1.4) when manganese was fed on the front end.

The need to supplement front end additives in this particular case is evidenced by the decreased pH at low load. Addition of both the powder cold end additive to one air preheater and the magnesium hydroxide slurry to the other yielded higher pH ash samples. The slurry was generally more effective at lower magnesium-oxide equivalent feed rates. Emphasis is placed on the ash pH measurements at low load and low RBU values because the dew point meter is less sensitive to chemical changes in this range.

This work and the data collected (Table I) show that the dew point meter can be very useful in selecting boiler operating conditions, evaluating additives, additive feed rates, etc. However, one should be aware of the meter's limitations. For example, measurements should be made before and after the air preheater because acid condensed on air heater exchange surfaces will not be detected if the probe is inserted downstream only.

If the alkali has sufficient time to react with the acid before reaching the dew point probe, the instrument will reflect it. However, in many cases neutralization occurs on the air preheater elements and cannot be detected by the dew point meter.

The relatively short and fixed length of the dew point probe makes it difficult to obtain a profile of the acid distribution in a duct. This is of significance in assessing the performance of cold end chemical additives because gas mixing can be surprisingly poor in those ducts.

Consequently, pH of fly ash samples taken after the air heater will then show if the chemical additive has neutralized sulfuric acid. Long years of experience have shown that when the ash pH is above about 3.5, sufficient acid has been neutralized to minimize corrosion problems and fouling of the air preheaters will not occur.

The results of this work demonstrate that dew point meters and fly ash sampling are viable tools for power plant operation to quickly evaluate both the potential for sulfuric acid corrosion and the effect of chemical treatment. This can be done in a short period of time so money is not needlessly spent for ineffective additives and more importantly, before severe corrosion and acidic stack discharges occur.

FIGURE 1 Probe For Collecting Oil Ash Samples For pH Determinations

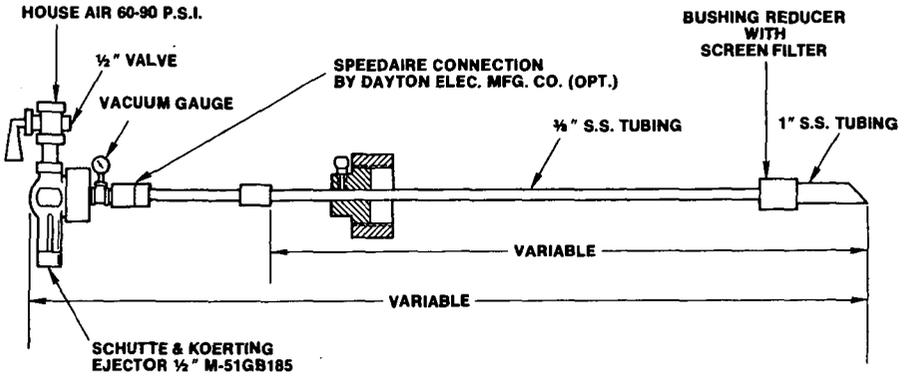


FIGURE 2

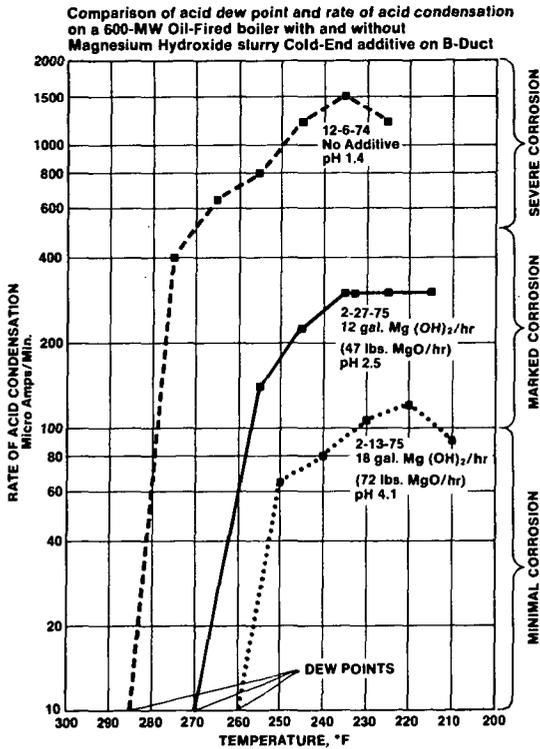


FIGURE 3

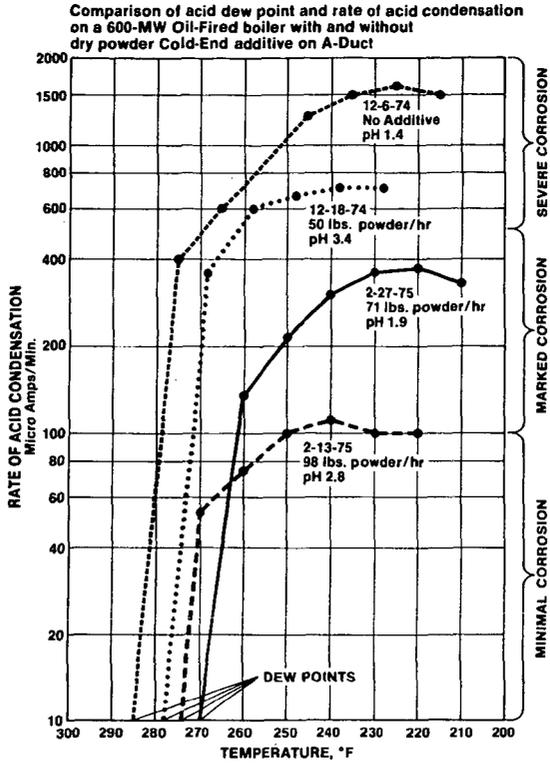


FIGURE 4

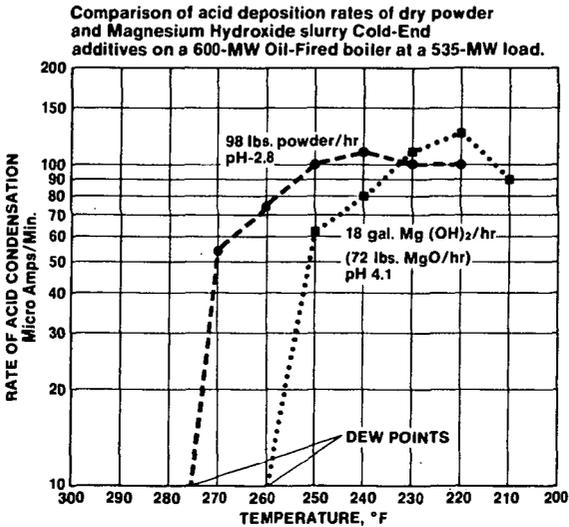


TABLE I

DEW POINT DATA AND ASH pH AS A FUNCTION OF ADDITIVE FEED ON A 600-MW OIL-FIRED BOILER

| Date | Fuel Oil Addty | MAGNESIUM HYDROXIDE SLURRY | | | | | | | | | | | | | | |
|----------|----------------|----------------------------|--------------|-----|----------------------|--------------|----------|--------|---------------------------------|--------------|-----|----------------------|--------------|-----|--------|------|
| | | POWDER ADDITIVE "A" DUCT | | | | | "B" DUCT | | | | | | | | | |
| | | Feed Rate (lb/hr) | Dew Point °C | °F | RBV (micro amps/min) | Peak Temp °C | °F | Ash pH | Feed Rate (gph) MgO Eqv (lb/hr) | Dew Point °C | °F | RBV (micro amps/min) | Peak Temp °C | °F | Ash pH | |
| 12-6-74 | Manganese | 0 | 141 | 285 | 1,600 | 107 | 225 | 1.4 | 0 | 0 | 141 | 285 | 1,500 | 116 | 235 | 1.4 |
| 12-18-74 | | -- | 137 | 278 | 725 | 114 | 238 | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 2-3-75 | | 68.5 | -- | -- | -- | -- | -- | -- | 0 | 0 | -- | -- | -- | -- | -- | 1.7 |
| 2-7-75 | | 41.7 | -- | -- | -- | -- | -- | 1.8 | 24.1 | 96.3 | -- | -- | -- | -- | -- | 4.1* |
| 2-9-75 | | 98 | -- | -- | -- | -- | -- | 2.8 | 16 | 64 | -- | -- | -- | -- | -- | 4.0 |
| 2-11-75 | | 98 | -- | -- | -- | -- | -- | -- | 18.2 | 72.7 | -- | -- | -- | -- | -- | 4.6 |
| 2-13-75 | | 98 | 137 | 278 | 118 | 116 | 240 | 2.8 | 18.2 | 72.7 | 127 | 260 | 126 | 104 | 220 | 4.1* |
| 2-27-75 | | 71 | 132 | 270 | 390 | 104 | 220 | 1.9* | 12 | 47 | 132 | 270 | 238 | 116 | 240 | 2.5* |
| 3-6-75 | | 50 | -- | -- | -- | -- | -- | 3.2 | 0 | 0 | -- | -- | -- | -- | -- | 2.3 |
| 5-15-75 | | 50 | -- | -- | -- | -- | -- | 3.2 | 16 | 64 | -- | -- | -- | -- | -- | 4.2 |
| 6-6-75 | Magnesium | 0 | 141 | 285 | 590 | 124 | 255 | 3.4 | 0 | 0 | 141 | 285 | 420 | 118 | 245 | 2.7 |
| 8-5-75 | plus Alum- | 0 | 141 | 285 | 108 | 106 | 222 | 2.4 | 0 | 0 | 141 | 285 | 135 | 106 | 223 | 2.4* |
| 8-6-75 | inum | 60-80 | 141 | 285 | 170 | 121 | 249 | 3.3* | 7-8 | 28-33 | 141 | 285 | 190 | 113 | 235 | 4.5* |

*Denotes data collected at low load operation -- 300-320MW. All data on 8-5-75 and 8-6-75 is on low load and compares two cold end treatments with Magnesium Oxide/Aluminum Hydroxide fuel oil additive.

Bruce L. Libutti, Ph. D.

Betz Laboratories, Incorporated
Trevose, Pennsylvania 19047

INTRODUCTION

When residual oil is burned, the sulfur it contains can cause many problems. These include pollution and localized problems of gas-side corrosion and deposition which can be especially severe when the fuel is burned in modern boilers which have heat recovery equipment. The additives and treatment programs discussed in this paper are designed to alleviate the localized problems.

Sulfur dioxide (SO_2) and sulfur trioxide (SO_3) are considered harmful pollutants, and acidic rain in which these gases are dissolved is aggressive to construction materials. Recently there has been much concern about the environmental effects of sulfates, which comprise the major part of the end products of sulfur oxides in the environment. (1) It is highly unlikely that a simple additive approach can remove enough sulfur oxides from flue gases to effectively alleviate the general SO_x pollution problem. Approaches which are now under active investigation by various companies and agencies include fluidized-bed combustion in a bed of limestone, dry limestone furnace injection, fuel pretreatment and wet scrubbers. (2, 3, 4, 5)

Localized corrosion, deposition and pollution problems can, however, be treated by an additive approach. These problems are all caused by acid condensation and commonly occur on the gas-side of the cold ends of boilers. The cold end of a boiler consists of the economizer, air heater, particle collection equipment and stack (Figure 1). Flue gas temperatures in this area typically range from 1200F to 200F. The air heater, where flue gas temperatures typically range from 600F to 350F, is the most common trouble spot. Sulfuric acid condenses on surfaces which are below the acid dewpoint and results in corrosion of those surfaces; resultant sticky deposits and exfoliated corrosion products can block the gas flow. Acid smut, which consists of soot particle agglomerates which have absorbed sulfuric acid, probably also forms on cooled surfaces. Emission of this material causes a major local pollution problem. In addition, hygroscopic, acidic fly ash is difficult to handle for disposal.

The cold-end additives developed by the work described here were developed to alleviate the problems of cold-end corrosion, cold-end fouling, acidic fly ash and acid smut. They will adsorb or react with SO_3 or sulfuric acid, rather than SO_2 .

By allowing boilers to run at lower exit gas temperatures without excessive cold-end problems, these additives should increase boiler efficiency and help save fuel.

The mechanism by which these materials alleviate cold-end problems was investigated and the influence of properties such as basicity, adsorptivity and particle size on additive effectiveness was studied. Knowledge of these factors is necessary to formulate and apply cold-end additives most efficiently.

Additive materials having a wide variety of properties were studied and are listed in Table I. Most were highly alkaline, but activated alumina and expanded vermiculite were moderately alkaline and were expected to be highly adsorptive; silica was expected to perform by adsorption alone. The particle size of all materials except sodium aluminate, sodium carbonate and vermiculite was 325 mesh or smaller. All of the materials are stable at cold-end temperatures except ammonium bicarbonate, which decomposes to yield ammonia, carbon dioxide and water.

TEST METHODS

Tests were conducted on three utility boilers and two industrial boilers, which ranged in capacity from 150,000 to 4,000,000 pounds of steam per hour. The utility boilers were equipped with Ljungstrom air heaters, and the industrial units had shell-and-tube air heaters. All were fired with no. 6 oil, with sulfur contents between 0.9 and 2.5 percent.

Additives were fed to points between the boiler economizers and air heaters where sufficient turbulence existed to insure even distribution across the duct. Test points were either upstream or downstream of the air heaters but were at least 10 feet downstream of the injection points. Additives were metered into pipes or headers leading to the ducts by a feeder consisting of a vibratory funnel and a vibrating trough, which was calibrated periodically using each additive. The additives were conveyed to the duct by gravity, boiler draft and when necessary, compressed air.

Tests were conducted to learn how additives affect acid deposition on surfaces. The rate of acid deposition was determined vs. surface temperature using a probe based on the British Central Electricity Research Laboratories (CERL) acid deposition probe.⁽⁶⁾ The probe washings were also analyzed for iron and total solids, which indicated corrosion rate and fouling tendency, respectively. Surface coverage was noted visually. An independent, indirect measure of acid deposition rate was obtained from a Land Instruments dewpoint meter, a commercial instrument. Gas flow rates and sulfur trioxide and sulfur dioxide concentrations in the flue gases were determined using a Research Appliance Corporation model 2343 stack sampling train.

The CERL probe was a stainless steel pipe, divided by rings into equal areas. A thermocouple was embedded in each area, and the pipe was fitted with an air-regulating valve. This probe was inserted in the boiler flue and cooled with compressed air. A temperature gradient along the length of the probe was obtained and recorded using the thermocouples. After exposure for a certain time, each area was washed with water, the washings were collected in separate bottles and titrated as sulfuric acid to determine the rate of acid deposition.

When using the Land meter, condensation of a conducting film of condensed acid on a controlled-temperature probe tip was detected by the onset of electric current flow between electrodes embedded in the tip. This allowed the apparent dewpoint to be determined, and comparative rates of acid build-up (RBU) were obtained from the rate of increase in current with time at any tip temperature.

The mechanism of cold-end protection by additives was discovered accidentally. Initial tests showed that additives had no effect on sulfur oxide concentrations in the flue gases. Additives were later found to reduce acid deposition on surfaces by coating these surfaces.

The test unit (Unit A) was a modern, front-fired utility boiler which was rated for 950,000 pounds of steam per hour. It was originally designed to burn pulverized coal, but was later converted to fire oil; specifically, it fired oil containing about 2.2 percent sulfur. As a result, the air heaters, which had been initially sized to handle large amounts of fly ash emanating from coal combustion, were improperly sized for flue gas from oil firing. The resulting low temperatures caused acid smut formation and a potential for acid corrosion.

Various blends of ammonium bicarbonate, adsorbents and alkali solids were injected upstream of the air heaters to try to neutralize SO_3 , but they had no effect on flue gas sulfur oxide concentrations or on the pH of fly ash from the precipitator hoppers. The mixing and residence times apparently were insufficient to effectively remove sulfur trioxide.

A second trial determined the effects of the additives on acid deposition on cooled surfaces. The additives were again injected into a turbulent area upstream of the air heater, and acid deposition rates were determined downstream of the air heater with the CERL probe. The additives were an alumina-silica mixture and an ammonium bicarbonate-silica mixture. At this time the plant had switched to a low-sulfur oil containing one percent sulfur.

Both additives effectively reduced acid deposition over a wide range of feedrates, as can be seen in Table II. The maximum additive: sulfur trioxide mole ratios represented by the feedrates in Table II were below 0.5:1 for both alumina and ammonia, as calculated from the measured flue gas flow rate and sulfur trioxide concentration. Stoichiometric reaction with SO_3 would have required additive: sulfur trioxide mole ratios of 0.33:1 for Al_2O_3 and 2:1 for ammonia.

The additives thus essentially eliminated acid deposition at dosages which were as low as one-fourth of stoichiometric, and reduced acid deposition at lower dosages. This fact, along with the negligible effect on bulk SO_3 concentration and the observation that a brief conditioning period was needed before the additive effects were seen, indicated that protection was resulting from coating the probe surface with additive rather than from reacting with the bulk of the sulfur trioxide. Ammonium bicarbonate apparently maintained its integrity long enough to reach the surfaces. It was thought that cold-end surfaces would be protected in the same way, and patent coverage⁽⁷⁾ was obtained for these additives.

There are several benefits of protection by surface coating. First and most obvious, a minimal amount of additive is needed since only the acid which condenses on surfaces is neutralized or adsorbed. Second, injection points can be chosen to solve specific problems such as air heater

corrosion or acidic, sticky ash in precipitator hoppers. Third, there is minimal effect on scrubbers or precipitators downstream since the bulk of the flue gas is unchanged.

CONFIRMATION

The beneficial effects of the additives applied in the manner described above were confirmed in trials at two utility boilers. Unit B burned no. 6 oil containing approximately 0.9 percent sulfur and produced 500,000 pounds of steam per hour; Unit C, fired with a blend of no. 2 and no. 6 oils containing about 1.2 percent sulfur, produced up to 4,000,000 pounds of steam per hour.

An ammonium bicarbonate-silica mixture effectively reduced acid deposition on the CERL probe in unit B at $\text{NH}_3:\text{SO}_2$ mole ratios of 1:1 and 0.5:1 (Figure 2). An alumina-silica mixture reduced the acid deposition rate on the CERL probe by approximately 50 percent and the initial corrosion rate of the probe by 30 percent in Unit C.

Further, indirect confirmation of the surface coating mechanism was provided by a partial failure in Unit D, an industrial power boiler which burned oil containing about 2.5 percent sulfur and produced approximately 600,000 pounds of steam per hour. The configuration of the shell-and-tube air heater is shown in Figure 3. Gas-side corrosion was occurring at the cold end of the air heater. An alumina-silica mixture was fed upstream of the air heater. Space limitations prevented CERL probe tests at the cone, but tests with the Land meter (Table III) showed that the alumina-silica additive depressed the apparent dewpoint and reduced the acid condensation. CERL probe tests at the cold-end of the air heater, however, showed no difference between treated and untreated flue gases. It was apparent that the additive was being lost in the 180-degree bend.

CORROSION TEST

The effectiveness of the alumina-silica mixture was confirmed by corrosion rate determinations in the cold end of a boiler producing 470,000 pounds of steam per hour (Unit E). Unit E fired blast furnace gas as primary fuel and coke oven gas and no. 6 oil as secondary fuels.

A corrosion specimen probe was constructed (Figure 4) and exposed to the flue gases after the air heater for 30 days without additive, and then for 30 days with the alumina-silica mixture being fed at a rate of six parts per million (ppm) by weight of flue gases. The surface temperature was 140F; the corrosion rate for the control, determined by specimen weight loss, was 52 mils per year (mpy). The corrosion rate for the treated gases was 32 mpy.

Visual inspection showed most corrosion to be on the downstream side of the specimen, which was inserted perpendicular to the gas flow. The additive had coated the leading surface of the specimen and effectively prevented corrosion.

ADDITIVE PROPERTIES

Once the surface coating mechanism was established, the effect of chemical and physical properties on cold-end additives was investigated. The

properties considered were alkalinity, adsorptivity and particle size.

The additives listed in table I were evaluated in an industrial boiler (Unit F) with a capacity of 150,000 pounds of steam per hour. The oil burned at this plant contained approximately 2.2 percent sulfur, and gas-side corrosion had caused perforation of the air heaters.

Only fine materials covered the CERL probe evenly, as visual inspection of the probe (Table IV) determined. This was confirmed by erratic acid deposition results for the coarse materials. For example, acid deposition rates for sodium aluminate differed by a factor of more than three. Such uneven coverage of cold-end surfaces would result in unreliable protection from acid attack and would lead to the danger of fouling air heaters before all surfaces were covered.

All five materials provided some protection, including one which did not neutralize the condensed acid.

Acid deposition rates on the CERL probe are shown in Figures 5 and 6, and rates of acid build-up on the Land meter are shown in Figure 7.

Figures 5 and 6 show that at high feedrates the alkaline materials MgO and Ca(OH)_2 were superior to the mildly alkaline $\text{Al}_2\text{O}_3\text{-SiO}_2$ combination; at lower feedrates all these materials were roughly equivalent. It may be that at high feedrates the basic oxides achieve some benefit from reacting with the bulk SO_3 , while at lower dosages surface-coating alone is operable and the materials are equivalent.

Figure 7 indicates that silica, which had no effect on acid deposition as measured by the CERL probe (Figure 5), did provide surface protection. Adsorbed but unreacted acid could be titrated in the CERL probe washings as free acid. The electric current increase measured by the dewpoint meter, however, depends on the formation of a continuous film on the probe tip. Adsorption by a non-conducting solid would prevent this.

Silica apparently did adsorb the condensing acid. Such adsorption would protect the surfaces by preventing contact with the acid. This was confirmed in an experiment when corrosion of the CERL probe (estimated from iron in the washings) was reduced 50 percent by allowing the probe to be coated by SiO_2 -treated flue gases for 90 minutes before starting the cooling air. The adsorptive, mildly alkaline alumina-silica combination looks especially good in Figure 7.

These additives do not cause fouling when applied properly. Analysis of CERL probe washings for total solids showed no increase in deposited solids in the presence of the additives: the reduced stickiness of the treated deposits probably counteracted the increased solids loading in the flue gases.

All the materials tested appear practical, except possibly calcium hydroxide which forms insoluble sulfates.

1. Cold-end surfaces may be protected by surface coatings of materials added directly to the cold end.
2. Protection by surface-coating offers advantages of economy and flexibility.
3. Fine particle size is essential in cold-end additives.
4. High adsorptivity and at least moderate alkalinity are desirable in cold-end additives.
5. Aluminum oxide, ammonium bicarbonate, magnesium oxide and silica are among the suitable materials for powdered cold-end additive constituents.

CURRENT PROGRESS

Blends of the various materials investigated in this study are available commercially. To insure maximum protection, suppliers must have expertise in additive application.

New materials now being tested include liquids, which should be especially convenient, and specific corrosion inhibitors.

With cooperation between boiler owners and operators and experts in fuel treatment, progress in energy conservation, equipment reliability and environmental quality can be furthered. Specifically, cold-end additives allow acid smut to be eliminated, prolong cold-end equipment life and increase boiler efficiency.

REFERENCES

1. Environmental Reporter, 5 (47), 1830 (1975).
2. R. C. Hoke, L. A. Ruth, and H. Shaw, Combustion, 46 (7), 6 (1975).
3. J. A. Alich, Jr., R. L. Dickenson, and N. Korens, Combustion, 46 (10), 8 (1975).
4. Combustion, 47 (4), 6-42 (1975).
5. Power Engineering, 79 (2), 26 (1975).
6. P. A. Alexander, R. S. Fielder, P. J. Jackson, and E. Raask, J. Inst. Fuel, 33, 31 (1960).
7. B. L. Libutti, Alumina as a Cold-End Additive, U. S. Patent No. 3,886,261, May 27, 1975.

TABLE I: ADDITIVE MATERIALS

| COMPOUND | ALKALINITY | PARTICLE SIZE |
|----------------------|----------------------|---------------|
| calcium hydroxide | high | 325 mesh |
| magnesium oxide | high | 325 mesh |
| sodium aluminate | high | coarse |
| sodium carbonate | high | coarse |
| ammonium bicarbonate | high (ammonia donor) | |
| activated alumina | moderate | 325 mesh |
| expanded vermiculite | moderate | 100 mesh |
| silica | low | submicron |

TABLE II: RATE OF ACID DEPOSITION: UNIT A

| Additive | Feeder Setting | Feed Rate | Acid deposition, $10^3 \times \text{mg H}_2\text{SO}_4$ $\times \text{min}^{-1} \times \text{in}^{-2}$ at temperature | | | |
|-----------------------------|----------------|-----------|--|------|------|------|
| | | | 360F | 300F | 240F | 180F |
| None | --- | --- | 2.1 | 7.4 | 12.2 | 15.4 |
| Ammonium bicarbonate-silica | 100% | 39lb/hr | 1.6 | 2.1 | 2.7 | 2.7 |
| | 70 | 27 | 1.6 | 1.6 | 2.7 | 3.2 |
| | 50 | 13 | 2.1 | 2.7 | 5.3 | 6.9 |
| | 40 | 4 | 2.1 | 3.2 | 4.3 | 5.3 |
| Alumina-silica | 100 | 13 | 2.1 | 3.2 | 4.3 | 5.3 |
| | 60 | 8.6 | 2.1 | 4.8 | 6.4 | 13.3 |
| | 50 | 2.6 | 2.1 | 3.7 | 6.4 | 8.0 |

TABLE III:
ACID DEPOSITION BY LAND METER, UNIT D CONE

| Feed Rate, lb Al_2O_3 - SiO_2 /hr | Dew Point, F | Temp of Max Rate of Acid Build-up, F | Maximum Rate of Acid Build-up, $\mu\text{amp}/\text{min}$ |
|---|-----------------|---|---|
| blank | 270 | 235 | 210 |
| 3.7 | 255-260 | 235 | 100 |
| 4.5 | 260 | 215 | 40 |
| 9.2 | 255 | 195 | 18 |

TABLE IV: SURFACE COVERAGE

| Additive | Coverage of CERL Probe |
|--|------------------------|
| SiO_2 | even (best) |
| MgO | even |
| $\text{Ca}(\text{OH})_2$ | even |
| vermiculite | spotty |
| Na aluminate | spotty |
| Na_2CO_3 | spotty |
| $\text{Al}_2\text{O}_3 + \text{SiO}_2$ | even |

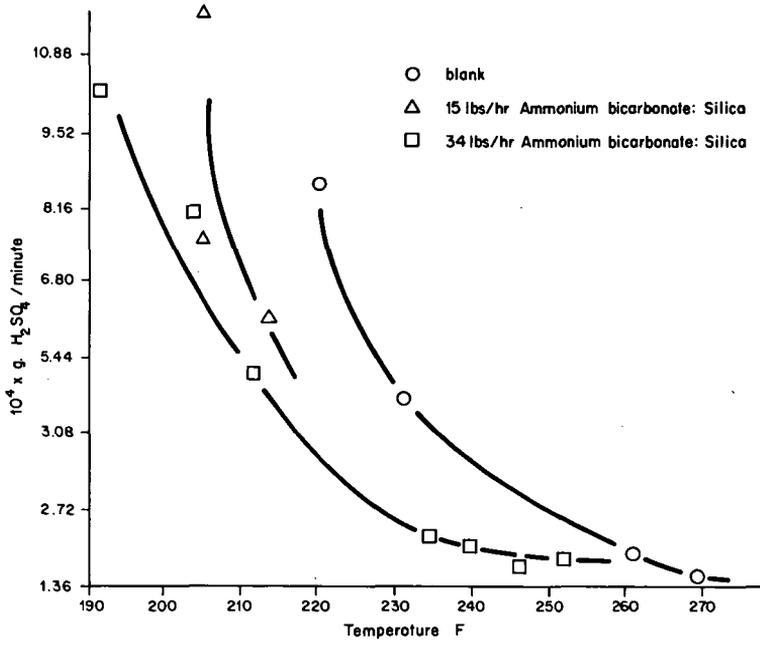


Figure 2. Acid Deposition; Unit B

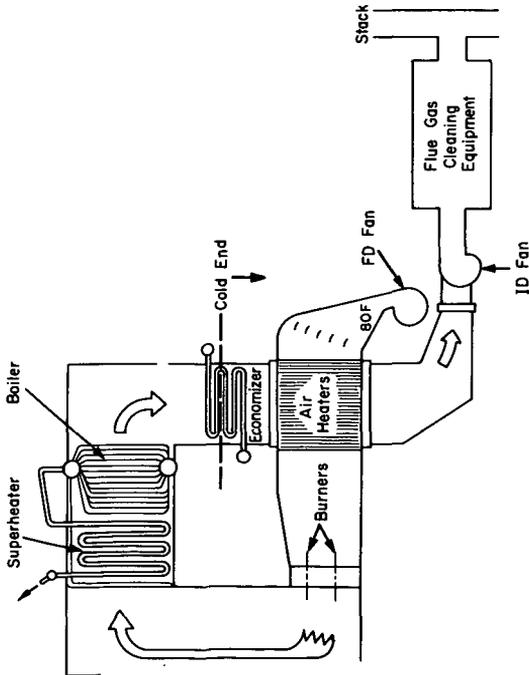


Figure 1. The Cold End

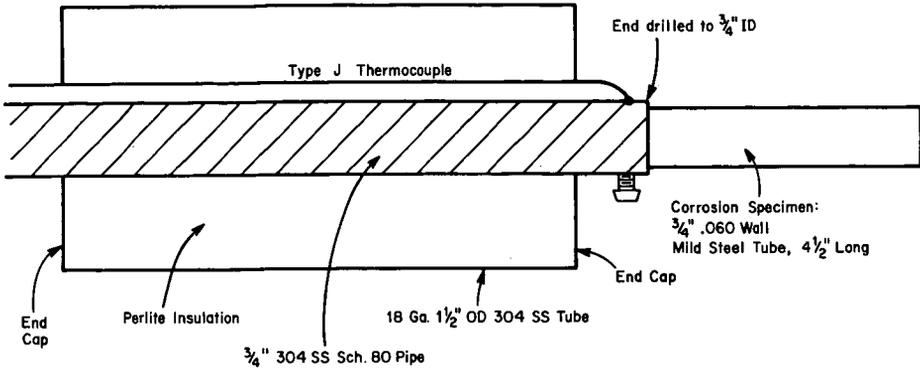


Figure 4. Corrosion Probe

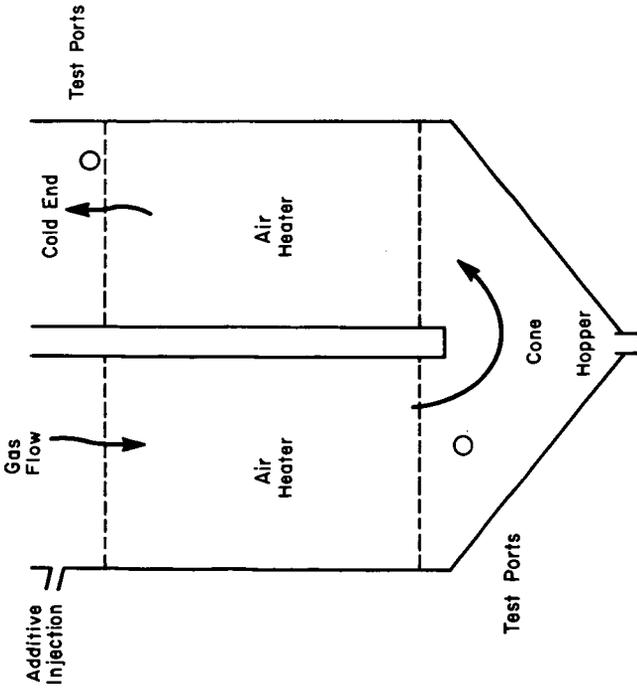


Figure 3. Air Heater Configuration, Unit D

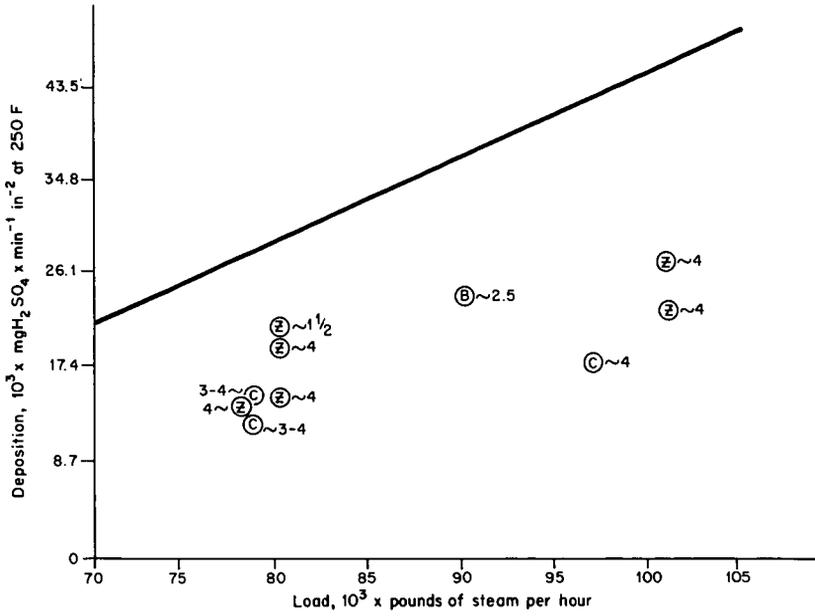


Figure 6. Acid Deposition, Low Feedrates, Unit F

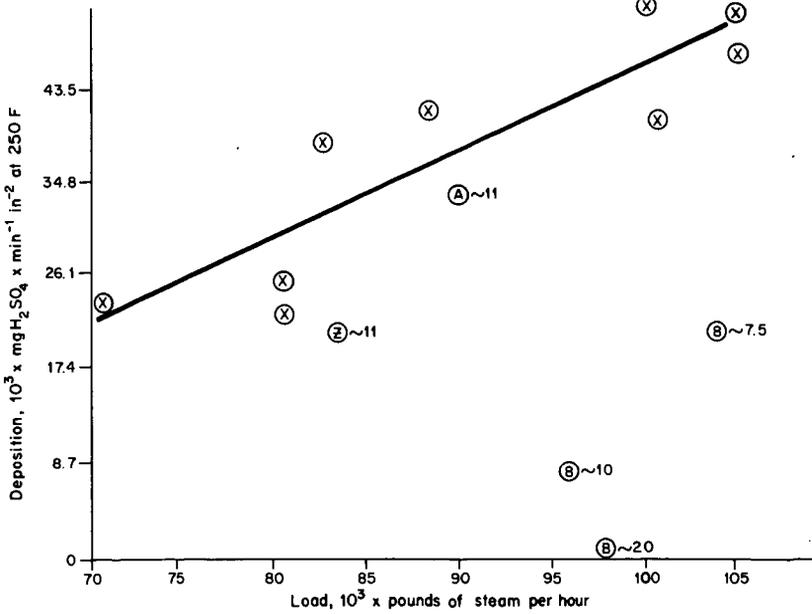


Figure 5. Acid Deposition, High Feedrates, Unit F

KEY TO FIGURES 5 and 6

| Symbol | Composition |
|--------|--|
| A | SiO_2 |
| B | MgO |
| C | Ca(OH)_2 |
| X | Control |
| Z | $\text{Al}_2\text{O}_3 + \text{SiO}_2$ |

_____ Control Runs

Feedrates as shown, in pounds per hour.

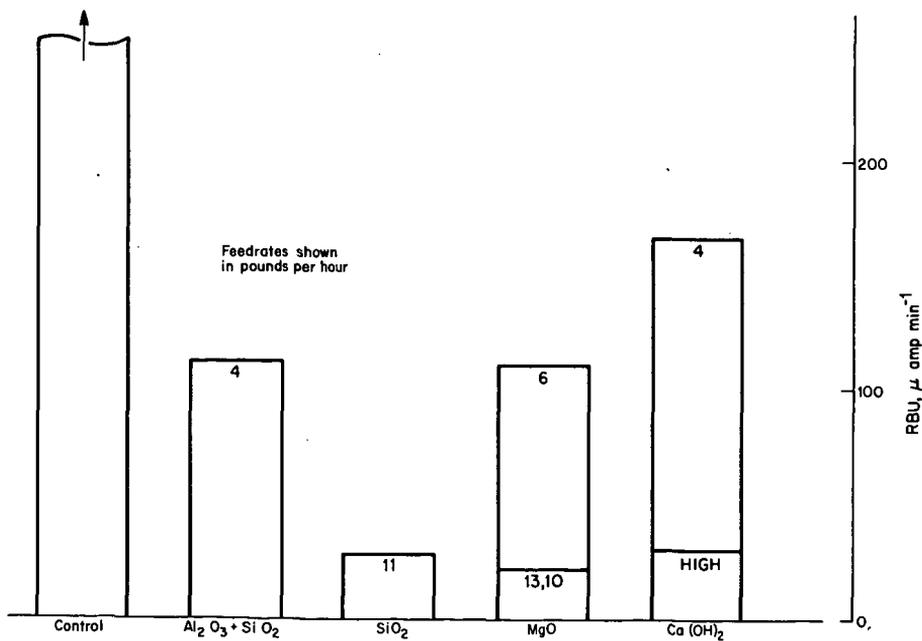


Figure 7. Rate of Acid Build-Up, Unit F

CHEMICAL REDUCTION OF SULFUR TRIOXIDE AND PARTICULATES FROM HEAVY OILS

Robert P. Bennett

Apollo Chemical Corporation, Whippany, New Jersey 07981

INTRODUCTION

There has been a significant increase in interest in the scientific application of fuel additives to residual fuel oils to solve fireside boiler problems, as well as additives to reduce air pollution from burning of residual fuels. This interest stems from: 1) restrictions on particulate and NO_x emissions imposed by the Environmental Protection Agency, 2) the higher price of fuel and the desire for increased efficiency, 3) the need to eliminate costly cold end corrosion, 4) community relations that require the eliminating of acid smut emissions and characteristic blue white plume caused by the condensation of SO_3 .

These fireside problems can be reduced or eliminated by instituting improved operating procedures plus the use of one or more additives added to the fuel oil or to the furnace burning the residual fuel.

Effective fuel additives have been shown to be limited to those that contain a metal. However, the choice of additive for any particular boiler depends upon the needs of the boiler and the particular environmental requirements.

In general, fuel additives should provide boiler cleanliness, high temperature vanadium corrosion protection, prevention of loss of operating capacity by maintaining design steam temperatures, cold end (air heater) corrosion protection, reduction of stack emissions from hydrocarbon particulate matter and SO_3 , and improvement in the handling characteristics of ash in the flue gas in oil-fired boilers equipped with precipitators and stack collectors. The significant fuel additives in use today usually contain MgO (with or without small amounts of aluminum oxide or hydrate), manganese, and MgO with manganese.

The use of magnesium oxide as a fuel additive, primarily for the control of vanadium slag, has been known for a number of years (1). The addition of MgO -based products to the fuel oil or furnace will raise the fusion point of the ash if used at a $\text{Mg}:\text{V}$ weight ratio of 1.5 to 1 (molar ratio of $\text{Mg}:\text{V}$ of 3:1). Properly treated ash will be soft, but voluminous. The increased ash burden on the boiler can lead to bridging and blockage in the boiler and increased particulate emissions. With today's low sulfur, low ash fuels, the use of MgO , at least as a slurry added to the fuel oil is no longer justified generally.

The purpose of this paper is to review the use of chemicals added to the fuel to improve combustion, thereby reducing unburned carbon particulate, and to reduce the formation of SO_3 in the flue gas, thereby reducing plume opacity and acid smut emissions.

Additionally, because additives in the fuel add to the ash burden of the boiler, an alternate approach for attacking the problems of cold end corrosion and acid smut emissions has been developed. This is a cold end feed of a properly constituted neutralizing additive, applied directly into the problem areas only and added strictly in proportion to the amount of SO_3 present in the flue gas, thus minimizing the treatment rate and reducing the problem of emissions to the atmosphere.

FUEL OIL TREATMENT

Sulfur in heavy fuel oil is oxidized readily to sulfur dioxide. A portion of this sulfur dioxide is further oxidized to sulfur trioxide. The extent of conversion of the SO_2 to SO_3 is dependent upon the percent of excess air and also on the presence of oxidation catalysts in the fuel, generally vanadium or nickel. Additionally, the boiler iron tube surfaces can themselves act as a catalyst for this reaction. The quantities of these catalysts will vary considerably in different fuel oils, so that the percent conversion, at any given level of excess air, will vary with the fuel and boiler cleanliness. It is difficult to predict the SO_3 content of the combustion products of a given fuel so, therefore, the exact dew point of the flue gas is difficult to forecast. An empirical correlation has been prepared as shown in Figure 1. It is similar to the experiences of others (2, 3, 6) who have shown the variation of SO_3 concentration as a function of O_2 concentration. Fuels examined have varied from a low vanadium content of below 50 parts per million up to fuels of 300 parts per million. Obviously, the best situation is to obtain the data for each particular unit. However, this graph has been extremely useful as a first approximation for a unit where test data are not available.

The sulfur content of the fuel oil obviously affects the parts per million of SO_3 in the flue gas. As expected, as the sulfur level of the fuel increases, so does the absolute amount of SO_3 in the flue gas up to a maximum level. Again, an empirical correlation of parts per million of SO_3 , in relation to the percent excess air and the sulfur in the fuel, can be obtained as shown in Figure 2. This also is similar to results of previous workers, such as Laxton (2), or Rendle et al. (7), both of whom used experimental furnaces. Note that a reduction in fuel sulfur from 2.5 to 1.5% results in a reduction in dew point of only about 7°F above an excess air of 10%.

From these two curves, it becomes obvious that in order to reduce SO_3 with any given fuel, the greatest effect would be obtained by reducing the percent excess air at which the unit is fired. Decreasing the excess air also has the advantage of decreasing BTU losses and increasing unit efficiency. However, excess air generally can only be reduced to a limited extent, before flue gas combustibles begin to increase rapidly. This in turn results in a decrease in efficiency or even unsafe firing conditions, as well as unsightly black plumes. The use of a combustion catalyst will reduce substantially the amount of combustibles in the flyash, and thus make it feasible to operate continuously at reduced or at low levels of excess oxygen. The latter in turn further reduces SO_3 generation.

An additional factor is that the use of a combustion catalyst, which is a metal, will also help to destroy the catalytic properties of the fuel metals by chemical reaction. Previous workers (1) have shown that operation at low excess air also favors the formation of the lower oxides of vanadium, V_2O_3 and V_2O_4 , which leads to high-melting ash and a minimum of corrosion and fouling.

The use of a manganese catalyst for the reduction of SO_3 is shown in Table 1. Note that at given oxygen levels (Units 2 and 3) there is a substantial reduction in SO_3 with treatment. The data for Unit 1 show both the reduction obtained from reduction of excess oxygen and the additional benefit of manganese treatment. The SO_3 content was determined by the well known EPA Method 8.

Particulate emissions consist of inorganic ash from the fuel, unburned carbon from incomplete combustion, and corrosion products. Flue gas ash loading from any particular fuel should be fairly constant at steady operating conditions. However, the carbon content can vary depending on the completeness of combustion and on excess air levels.

A number of metals are known to be effective as combustion catalysts. They can reduce particulate loadings if they promote more complete burning of the carbon portion. A recent paper by Giammar (4) points out the effectiveness of manganese for this purpose. It has been found that manganese can be used as an inorganic slurry (5,10) or in the form of a truly soluble organometallic species. The inorganic type is most economical for use in heavy fuels where higher concentrations of manganese are required, as compared to distillate fuels.

In a typical example, a refinery was required to burn heavy asphaltic bottoms in a package boiler producing 200,000 lbs. of steam per hour at 900°F superheat temperature and 900 psi. superheat pressure. Treatment of the pitch with 45 ppm Mn produced a decrease in flue gas particulates from 0.17 to 0.04 mg/SCF with a corresponding reduction of carbon content of the particulate from 72% to 31%.

For gas turbines and package boilers, the soluble form often becomes the additive of choice because of the ease in handling, particularly since the requisite parts per million of manganese is low enough so that the extra cost for supplying a soluble form of manganese is considered to be economical.

In addition to the reduction in acidic emissions and particulate emissions obtained by the use of a manganese combustion catalyst and reduced excess air level operations, there is often a significant increase in efficiency obtained. This can be directly translated into fuel savings and dollars as shown in Table 2. This efficiency increase alone often justifies the use of a fuel additive.

COLD END TREATMENT

So far, we have described the benefits of using fuel additives to reduce SO₃ emissions and to decrease unburned carbon particulate emissions. Even with these treatments, it has been found that a number of units suffer from varying degrees of cold end corrosion with resulting air heater blockage and wastage. Even with low sulfur fuels, many units experience cold end problems.

To minimize these problems one can reduce SO₃ content totally or raise the exit gas temperature above the dew point. Two methods of doing the latter are available: 1) steam coils in the air duct upstream of the air heater can be used to raise the temperature of the incoming air for combustion. This results in a higher metal temperature at the cold end of the air heater. 2) An air heater by-pass damper upstream of the air heater can be used to by-pass a portion of the incoming air for combustion around the air heater. This also results in a higher temperature at the cold end of the air heater. Both of these methods raise the exit gas temperature and sacrifice unit efficiency. A 40°F change in exit gas temperature is generally equivalent to 1% in unit efficiency.

An alternate, or supplementary treatment, depending on boiler operations, is the injection of a cold end, free-flowing, neutralizing powder (8), a process (10) which has been perfected over several years. This material is usually applied after the economizer and has the advantage of only being added in proportion to the free SO₃ present. In this way, the acidic conditions are neutralized with minimum burden on the system.

To illustrate the success of this approach, let us consider several case histories.

EXAMPLE I

A 220 MW pressurized unit with a Ljungstrom air heater had both severe corrosion and air heater pluggage problems which required a high exit gas temperature of 300°F to protect the cold end. The #6 fuel oil contained 400 ppm vanadium and 2.5% sulfur. Fuel use rate was 302 bbl./hour or 12,684 gallons per hour. MgO, in the form of a slurry, was added to the fuel oil in an attempt to solve the corrosion and pluggage problems and acid smut emissions. This approach was unsuccessful because of excess ash and blockage within the boiler. It was therefore decided to try cold end feed. The acid dew point of the untreated unit was 300°F, whereas the exit gas temperature was only 305°F. Using a feed rate of neutralizing agent of 0.19 lbs./bbl., the dew point was reduced to 180°F or essentially a water dew point. This allowed a safe reduction in exit gas temperature to 265°F by shutting off steam air preheaters and closing air heater by-pass ducts. The economic gain from these features alone was over \$200,000 annually. Additional benefits were reduced corrosion and maintenance costs and improved unit performance because of no air heater pluggage with treatment.

During the course of this investigation, we were again able to demonstrate that just the reduction in excess air alone is not sufficient to reduce the SO₃ to a low enough level to protect the cold end of the unit. Figure 3 shows the effect of excess air reduction on SO₃ generation in the untreated unit at constant load. Dropping the excess air level from 12 to 5% reduced the SO₃ content from 80 ppm to 30 ppm, but still resulted in a dew point of 290°F. Treatment with additive at 12% air reduced the SO₃ to 16 ppm and reduction to 5% air at the same treatment rate reduced the SO₃ to 2 ppm allowing safe operation at an exit gas temperature of only 265°F.

In considering a safe exit gas temperature, it must be remembered that it is not just the average cold end metal temperature, but the minimum metal temperature under the poorest operating temperatures and the duration of these conditions against which protection must be provided. By the use of the neutralizing additive, one not only stops the corrosion completely, but often also picks up the added economic benefits of being able to safely turn off water or steam air heaters and/or close air heater by-pass dampers.

EXAMPLE II

Even with low sulfur fuel (0.3%), units which cannot reduce excess air levels have a need for cold end protection. For example, a 350 MW pressurized boiler with a Ljungstrom air heater was experiencing significant cold end corrosion. This unit burned #6 oil of about 14 ppm vanadium and 0.3% sulfur. Excess air was 15%. Fuel consumption was 600 bbls./hr. or 25,200 gallons per hour. The exit gas temperature was 270°F, but the acid dew point was 273°F, equivalent to 10 ppm_v of SO₃. By applying the powdered neutralizing agent to the cold end ahead of the air heaters at a rate of 0.033 lbs./bbl, the dew point was reduced to 150°F or 0 ppm_v SO₃. By shutting the by-pass dampers, a 30°F reduction in exit gas temperature could be safely achieved. Fuel consumption alone has been cut by 14,000 bbls. a year, which at current prices is a savings of \$182,000.

CONCLUSIONS

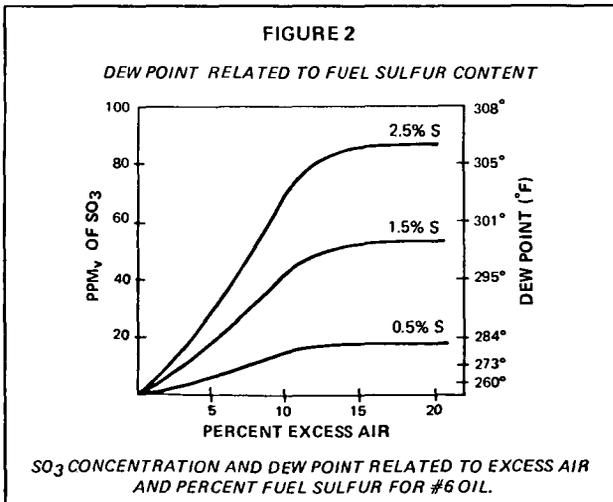
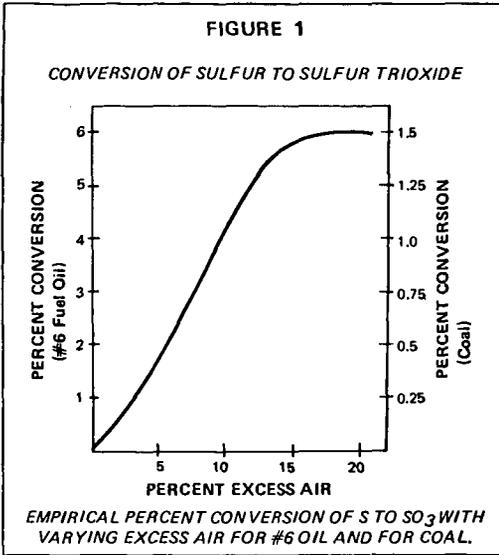
In summary, we have reviewed the production of SO_3 and unburned particulate from burning heavy oils. Formation of SO_3 leads to corrosion of the cooler parts of the boiler, such as the air heater and duct work, and can produce a visible plume and acidic emissions. Unburned particulate leads to excessive emissions and a visible plume. Mechanical corrections alone usually are not sufficient to eliminate these problems. The use of a manganese combustion catalyst allows operation at low excess air levels, and consequently low SO_3 levels, without the adverse formation of unburned carbon particulate matter. The use of lower excess air levels improves unit efficiency and saves fuel.

Additionally, neutralization of residual SO_3 by application of a neutralizing additive in powder form into the cold end of the boiler allows operation at lower flue gas temperatures because of the lowered acid dew point. Air heaters and cold end duct work are thus protected while lower exit gas temperatures improve unit efficiency.

The combination of these two approaches: the use of chemical in the hot end for combustion improvement, and chemical in the cold end for acid neutralization, leads to significant savings with heavy fuel oil units while at the same time minimizing or eliminating emissions problems (9).

REFERENCES

1. Reid, W. T., "External Corrosion and Deposits," American Elsevier, New York, New York, 1971.
2. Laxton, J. W., in "The Mechanism of Corrosion by Fuel Impurities," Butterworths, London, 1963, pp. 228-237.
3. Reese, J. T., Jonakin, J., and Caracristi, V. Z., Combustion, 36, 29, (1964).
4. Giammar, R. D., Krause, H. H., Locklin, D. W., ASME, 75-WA/CD-7.
5. Kukin, I., "Effects of Additives on Boiler Cleanliness and Particulate Emissions," International Meeting of the Society of Engineering Science, Tel Aviv, Israel, June 1972.
6. Kukin, I., and Bennett, R. P., "Chemical Reduction of SO_3 , Particulates and NO_x Emissions," The International Energy Engineering Congress, Chicago, Illinois, November 1975.
7. Rendle, L. K., Wilsdon, R. D., and Whittingham, G., Combustion, 31, 30, (1959)
8. Kukin, I., and Ross, A., Combustion, 45, 14, (1974).
9. U.S. Patent 3,837,820.
10. U.S. Patent 3,692,503.



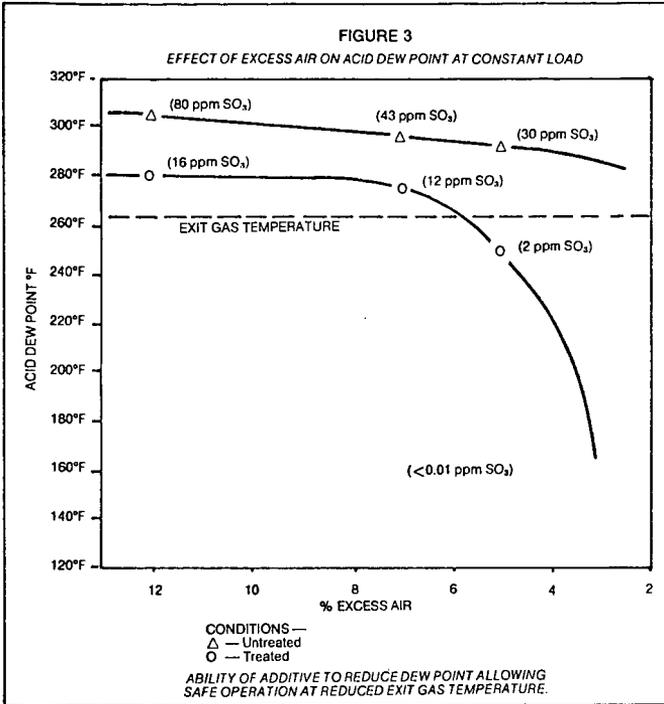


TABLE 1

EFFECT OF MANGANESE ON SO₃ GENERATION

| Unit | % O ₂ | SO ₃ (PPM at 3% O ₂) | | Percent Reduction |
|------|------------------|---|---------|-------------------|
| | | Untreated | Treated | |
| 1 | 1.2 | 9.1 | 5.0 | 45.1 |
| | 1.7 | 14.2 | 8.0 | 43.7 |
| | 2.2 | 20.4 | 9.0 | 55.9 |
| 2 | 4.5 [±] | 2.5 | 1.7 | 32.0 |
| 3 | 7.4 | 15.0 | 9.0 | 40.0 |

ABILITY OF MANGANESE TO REDUCE SO₃ CONCENTRATION IN DIFFERENT UNITS AT VARIOUS EXCESS AIR LEVELS.

TABLE 2

FUEL SAVINGS FROM REDUCTION OF EXCESS AIR ALLOWED BY USE OF MANGANESE ADDITIVES

| | |
|--------------------|--|
| Unit: | 100 MW |
| Fuel: | #6 fuel oil with a heat value of 18,500 BTU/lb. |
| Fuel Use Rate: | Average 52,500 gallons/day |
| Excess Air: | 30% Initial: 18.50 lbs. air/lb. of fuel 8% Final: 15.73 lbs. air/lb. of fuel/diff. = 2.77 lbs air |
| Additive: | 31% Mn slurry at rate of 1 gallon/12,000 gallons fuel |
| Heat Capacity: | 0.237 BTU/lb. of air/°F |
| Average Heat Loss: | Air to preheater = 85°F (ambient) Exit gas temp. = 275°F (average) ΔT = 190°F |
| BTU Savings: | {2.77 lbs. air/lb. fuel} (0.237 BTU/lb. air/°F) (190°F) = 124.7 BTU/lb. fuel oil Oil consumed (avg.) = 52,500 gal./day @ 8 lbs./gal. = 420,000 lbs./day @ 124.7 BTU/lb. = 52,374,000 BTU/day (saved) |
| Fuel Saved: | 52,374 x 10 ⁶ BTU/day = 353.88 gal/day (saved) 148,000 BTU/gal. = 8.42 bbl./day At current price of \$11/bbl., this is worth \$92.62/day. |

AND IMPACT ON THE U. S.

By Kolluru Rao and Irving Skeist

Skeist Laboratories, Inc.
112 Naylor Avenue
Livingston, N. J. 07039

Ammonia and other nitrogenous fertilizers are an essential ingredient of the Green Revolution, which ushered in high yielding varieties (HYV) of grain highly responsive to plant nutrient usage.

China and India are the largest nitrogen (N) consumers among the less developed countries, and rank third and fourth in the world. Production of N in India and China is 2 million tons short of demand; both have embarked on ambitious programs to build up domestic synthetic ammonia capacity. While China is expected to reach near self-sufficiency by 1980, India will continue to be in deficit by nearly one million tons of N nutrient.

The imbalance in demand-supply could be alleviated by fuller utilization of existing capacity (which in India has been only 55% employed), improvements in packaging and distribution, balanced agricultural inputs, selection of appropriate nutrient form and NPK ratios, and import of food and fertilizer. Longer term measures include natural and biological means of fixing nitrogen employing symbiotic or asymbiotic relationships with nitrogen-fixing organisms, a shift away from grains toward high-protein legumes (which naturally fix 35 million tons of N worldwide), and population planning.

Coal has lately become the focus of interest as a raw material for ammonia. In a recent comprehensive study on Coal Chemicals by Skeist Laboratories, we find that coal becomes a viable alternative to OPEC oil or decontrolled natural gas under certain conditions. Furthermore, the selection of appropriate coal conversion process or technology is critical as it would lead to difference of 20% or more in operating rate and ammonia production cost. As early as mid-1960s, India launched a program to base a million tons of ammonia on coal.

But synthetic fertilizer capacity is highly capital intensive and could be a huge drain on the foreign exchange resources of a developing country. The current rate of increase in India's population dictates one 1,500 tons/day ammonia plant requiring an investment of \$200 MM, coming on stream each year. We expound in this paper an alternative -- the fuller and optimal exploitation of a resource indigenous to India -- the cattle dung. The proposed dung gas system is designed to meet the twin needs of a farmer; it yields manure rich in NPK (3-5% of dung input) and bio-gas (2,000 CF or 1.1 MM Btu/ton dung processed) for cooking and other fuel applications. If 100 million tons of cattle dung were processed in dung plants, such as the ones discussed here, the output in terms of N alone would be equivalent to 3.3 million tons urea (1.5 MM tons N) or \$900 million at current prices. The value of fertilizer plus gas approaches \$2 billion per year.

Such a plan would bridge the gap between projected demand and supply, not only in fertilizer but also in food, and could potentially support a population growth of 100 million people.

Demand/Supply of Nitrogen

The introduction of HYV in the late 1960s accentuated the need for fertilizers. Of the three plant nutrients, nitrogen, P₂O₅, and K₂O, the nitrogen is by far the most critical, particularly in Asia because of the cropping patterns. Nitrogen, mostly in the form of urea and ammonium nitrate, represents two-thirds of the 15.5

Nitrogen production and demand for India, Asia and the world are shown in Table 1. Nutrient consumption in India quadrupled in less than a decade, exceeding 2.8 million tons in 1974-75, of which N made up 2 million tons. Even so, NPK usage amounted to only 15-16 kg/ha compared with 440 in Japan, 82 in the U.S., 40 in China and 41 in the Punjab State of India. Thus, there are wide disparities not only between the developed and the less-developed countries but also among the latter, and even in a country.

Asia's N consumption, currently 24% of the world's total, is expected to go up to 26% in 1980. India and China have combined usage of 6 million tons N -- 60% of Asian market. The Asian market is more or less in balance, thanks to Japan's more than 2 million tons of surplus production. Following massive build-up of N capacity over the next 5 years in China, India and Indonesia as well as the Mideast, Asia's demand/supply should be in balance by 1980 even without Japan's surplus, turning the continent into a net exporter. But India's domestic supply of N will still be a million tons short of demand, making her as the world's largest deficit country. (The merits of domestic production vs. imports in dealing with the deficit are discussed later).

Table 1. Nitrogen Fertilizer Production* and Demand 1970-1980
Million Metric Tons of Nitrogen (N)

| | I n d i a | | | Asia | | Asia excl. Japan | | World |
|------|-----------|------|---------------------|------|------|------------------|------|-------|
| | P | D | Imports/ Deficit | P | D | P | D | |
| | | | | | | | | |
| 1970 | 0.71 | 1.36 | 0.65 | 5.1 | 6.5 | 3.0 | 5.6 | 30 |
| 1971 | 0.84 | 1.49 | 0.65 | 5.6 | 7.2 | 3.5 | 6.3 | 33 |
| 1972 | 0.95 | 1.76 | 0.81 | 6.5 | 7.4 | 4.4 | 6.7 | 35 |
| 1973 | 1.1 | 1.78 | 0.68 | 7.7 | 8.2 | 5.2 | 7.4 | 38 |
| 1974 | 1.1 | 1.78 | 0.68 | 8.1 | 9.2 | 5.0 | 8.4 | 41 |
| 1975 | 1.7 | 2.0 | 0.3 | 9.8 | 10.0 | 6.7 | 9.2 | 42 |
| 1976 | 2.2 | 2.7 | 0.5 | 10.4 | 10.9 | 7.3 | 10.0 | 45 |
| 1977 | 2.7 | 3.0 | 0.3 | 11.9 | 11.8 | 8.8 | 11.0 | 48 |
| 1978 | 2.7 | 3.3 | 0.6 | 13.3 | 12.8 | 10.2 | 12.0 | 51 |
| 1979 | 2.8 | 3.6 | 0.8 | 15.7 | 13.8 | 12.6 | 13.0 | 54 |
| 1980 | 3.0 | 4.0 | 1.0 | 17.0 | 14.8 | 14.0 | 14.0 | 57 |

*Nonagricultural capacity ranging 10-25% excluded. Projections for 1975-1980 are based on 70% capacity utilization in Asia, including India, from the third year of a new plant operation.

Forecasts of fertilizer demand in India and other 'non-free market' countries must be qualified. Demand is often constrained by supply. Demand is a function of the cost of fertilizer, purchasing power of farmer and the country, crop prices, timing of application, average land holding, population growth and governmental incentives. A rule of thumb estimate of fertilizer requirement can be made in terms of population growth -- one ton nutrient for 10-15 tons incremental food, sufficient for 30 people per year. Another measure is the optimum rate of fertilizer application. The recommended rate of N for HYV is 100 kg/ha vs. actual use of 42 for rice and 31 for wheat in India. In the case of traditional varieties, the recommended rate is 40-50 kg/ha, in contrast to actual use of 6 for rice and 14 for wheat. Overall nitrogen average in India has been 10 kg/ha, bringing into focus the sizable potential demand and elasticity. The projected demands for India and Asia of 4 and 15 million tons N in 1980 could consequently turn out to be very much on the conservative side.

Measures to Cope with Ammonia Shortages

Short-Term measures include:

- fuller utilization of existing capacity, which has been operating in the 40-70% range in many non-industrial countries, and about 55% in India, owing to power cuts, raw material difficulties and poor maintenance. Newer plants are operating at 70% or higher; at 90-100% India could be self-sufficient in N today. Moreover, the production cost of NH_3 is sensitive to operating rate; increasing it from 70% to, say, 90% would result in 25% lower price.

- improvements in packaging, storage, shipping and handling. These operations account for more than 50% of the cost to the farmer. Freight on urea from Osaka, Japan to Bombay, India, for example, costs only \$29/ton in bulk vs. \$42 bagged. Further, the choice of high concentration nitrogenous fertilizers like ammonia and urea should lower distribution costs.

- choice of right fertilizers. Urea or ammonium phosphate is more effective for rice fertilization than the nitrate form. Liquid and gaseous fertilizers including aqueous and anhydrous ammonia, nitrogen solutions and NPK solutions are generally more economical than traditional solid forms.

- imports; joint ventures.

Long-term measures include:

- nitrogen fixation, chemical or biological.

- changes in dietary habits, shifting emphasis from cereals to legumes capable of fixing nitrogen from the air. World legume production amounts to 120 million tons, about 10% of cereal grains. Worldwide, the amount of naturally fixed N in high protein legumes like soybeans and peanuts is estimated at 35 million tons in 1975, comparable to the 42 million tons of synthetic N nutrient.

- development of techniques to improve N recovery and utilization from fertilizers, which at present averages only 50% by crops.

- population planning.

Imports vs. Domestic Production

Synthetic ammonia is the source for more than 90% of nitrogenous fertilizers in the world. Natural deposits, organic waste materials and coke-oven by-product make up the remainder.

The most desirable feedstock for ammonia synthesis is natural gas (methane), followed by naphtha, heavy oil and coal. Among the most populous countries of Asia, Indonesia and China have adequate reserves of natural gas and oil to form the basis of a large domestic fertilizer industry. China's natural gas reserves, according to TVA estimates, will support twenty-one 1,000 mtpd (7 million tons/yr) ammonia plants consuming 25% of the reserves. Both Japan and India are heavily dependent on imported high cost naphtha -- the backbone of their fertilizer industry.

In an attempt to reduce dependence on imported naphtha and the foreign exchange component of NH_3 , India has turned to coal recourse, even though plant investment for coal is 50-60% higher than for naphtha reforming. Three 900 mtpd NH_3 plants based on Koppers-Totzek coal gasification are under construction, and could furnish nearly one million tons of ammonia per year. In fact, a small 300 mtpd Winkler plant gasifying lignite has been operating since the early 1960s. Experiments are also in progress to use ammoniated coal for fertilizer.

India may also examine the possibility of importing LNG from Mideast. Abu Dhabi, separated from India by no more than 2,000 miles of water, flares 10 billion cubic meters of gas -- sufficient to produce 10 million tons of NH_3 . Importing LNG would of course require investment in cryogenic tankers and special storage and handling equipment. India is reported to be actively considering a \$300 million joint ammonia

Alternatives

Some of the alternatives for a country deficient in feedstocks and food are presented in Table 2.

Table 2. Relative Economics of Food vs. Fertilizer - Imports and Domestic Production (Developing country importing raw materials)

| | Rice | Wheat |
|--|----------|-------|
| Cereal price, \$/kg | 0.40 | 0.17 |
| N cost, \$/kg (\$275/ton urea mid-1975, India) | 0.60 | 0.60 |
| Incremental food production, kg, by application of 1 kg nutrient (Response ratio) | 15 | 10-12 |
| Value of incremental food, \$ | 6 | 2 |
| Food/Nutrient cost ratio | 10 | 3-4 |
| Population supported by 1 ton nutrient/year** | 30 | 20-25 |
| New investment in domestic production* | | |
| Plant investment, 1,000 mtpd ammonia from naphtha | \$125 MM | |
| Ammonia production cost | \$175/mt | |
| Raw material cost % of nutrient (N) cost | 46% | |
| Ammonia selling price with 20% ROI | \$250/mt | |
| Raw material cost % of nutrient (N) price | 32% | |

* Total plant investment for 1,000 mtpd ammonia based on naphtha reforming is reported to be \$125-130 MM, and production cost \$175/mt at 90% operating rate. ROI at 20% translates to a sales price of \$250/mt ammonia or \$305 mt. N. Imported naphtha is assumed at \$90/mt; 0.88 tons naphtha required per ton NH₃ or 1.073 tons (\$97)/ton N.

**One ton grain supplies 5,000 cal/day for one year - sufficient for 2 people at an average 2,500 cal/day per capita.

Clearly, it is far more desirable to import plant nutrient than food. Typical ratios of food/nutrient costs are 3-4 for wheat and 10 for rice. The economics of raw material imports generally appear to be more favorable than fertilizer imports; however, the advantage is not always decisive. Feedstock makes up nearly one-half N production cost, excluding ROI, at \$90/ton imported naphtha. While it is reasonable for a developing country to want to achieve self-sufficiency in fertilizers, it is questionable whether a no-imports policy, and the investment it entails, represents optimum allocation of resources.

Impact on U.S. Exports

As a result of heavy investment in NH₃ capacity all over the world, most countries that are importers now will either achieve self-sufficiency (e.g. Latin America) or become exporters by 1980 (Indonesia). In the Mideast, Iran and Kuwait are expected to have 1/2 million tons of N for export. Indonesian industry, operating at a remarkable 100% level, should have another 1/2 million tons for export. No significant increase in capacity or demand is foreseen for Japan, and she will continue to look for overseas markets for 2 million tons of surplus product. Heavy construction is also reported in Russia, presumably with the objective of doubling by early 1980s its present capacity of 12 million tons of ammonia. Western Europe will probably have 1 million ton nitrogen surplus.

It appears, therefore, that American N exports will be facing increasingly tough competition. In any event, the opportunities for American engineering companies for sale of technology and equipment are indeed impressive - as exemplified by M. W. Kellogg which reportedly has contracts for eight 1,000 tpd ammonia plants in China alone.

The cattle dung gas plant, illustrated in Figure 1, is a simple but ingenious device that integrates and 'optimizes' the production of fertilizer and fuel - the two essential commodities for the farmer.

The equipment consists of a fermentation well or digester, a gas holder and an inlet tank and an outlet tank connected by pipes. The cylindrical fermentation well is below ground level, lined with brick and mortar. The gas holder is made of mild steel or fiberglass reinforced polyester.

Cattle dung and other organic material mixed with equal volume of water and urine is fed to the inlet tank in a slurry. An equal amount of fermented slurry, minus about one-fourth converted to gas, flows out into the compost pit or outlet tank. Initially the fermentation well is completely filled with slurry; it takes about 10 days for enough gas to be generated to fill the holder. The outlet tank is located below the level of the inlet tank to achieve the necessary pressure balance. The pressure of gas collected in the gas holder is equal to the weight of the holder. A pipe connects the gas holder to kitchen or nearby points where gas would be utilized.

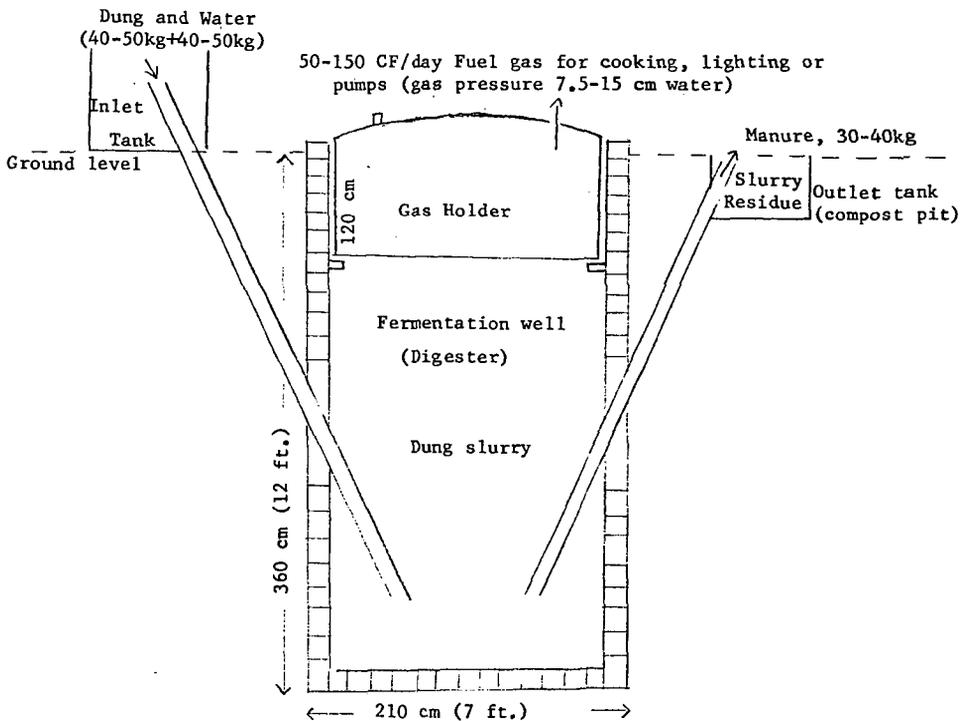


Figure 1. Cattle Dung Bio-gas Scheme - 100 CF Gas/day (3 cm/d; not drawn to scale)

Table 3. Inputs and Products of 100 CFD Dung Gas Plant

Inputs:

40-50 kg/day (for 100 CF Gas)
 (Cattle dung mixed with equal amounts of water and cattle waste).

Every 100 CF gas capacity requires dung of at least 4-5 animals. Dung averages at 10 kg/day per adult cow or bullock and 14 kg per buffalo on site. The availability of dung for conversion may in fact be substantially lower, as the cattle are not always stable bound.

Outputs:

1. Gas: 1-3 CF/kg of fresh dung

| <u>Composition</u> | <u>Vol. %</u> |
|--------------------|---------------|
| CH ₄ | 50-60 |
| H ₂ | 5-10 |
| CO ₂ | 30-45 |
| N ₂ | 1-2 |
| H ₂ S | Traces |

Heating Value: 550 Btu/CF

Typical gas requirements:

| | | |
|-------------|---|---------------------|
| Cooking | - | 12-15 CF/person/day |
| Electricity | - | 22 CF/KWH |
| Gas engines | - | 15-16 CF/HP-Hr |

2. Slurry residue/manure product 75-80% of dung input (remainder turns into gas)

| <u>Nutrient</u> | <u>Content on dry basis</u> |
|---|-----------------------------|
| Nitrogen N | 1.5-2% |
| Phosphate P ₂ O ₅ | 1 - 2 |
| Potash K ₂ O | 1 |

Economics

Capital investment and operating costs of 100 CF/day gas plant and estimated value of products are as follows:

Capital investment

| | | |
|--------------|---|-------|
| Equipment | - | \$120 |
| Construction | - | \$140 |
| | | \$260 |

Annual operating costs*

| | | |
|---|--|-----------|
| Maintenance (paint) | | \$10 |
| Interest at 10% on 75% of investment (25% gov't. grant) | | 20 |
| Depreciation (15 yrs) | | <u>17</u> |
| | | \$47 |

Value of Products

| | | |
|--|---|------------------|
| Gas: (100 CFD) x (360) = 36 MCF - 20 MM Btu/yr | | |
| @ \$1.25/MCF (\$2.27/MM Btu) | = | \$45 |
| Manure (NPK < 5%) approx. 15 tons | | |
| @ \$5/ton | = | <u>\$75</u> |
| Total value | | \$120/yr. |

* Excluding the cost of labor of owner-operator.

Return on Investment

$$\text{ROI} = \frac{\text{Average yearly profit}}{\text{Original fixed investment} + \text{working capital}} = \frac{73}{(260 \times 0.75) + 0} = 37\%$$

The 37% ROI or 3 year payoff period is attractive. But even the small investment could strain the resources of an Indian farmer; the government therefore provides 25% grant as an inducement and the balance on loan.

The size of dung unit is determined by the number of cattle and fuel and fertilizer needs. A range of 100-300 CFD is common but there is no reason why, say 5,000 CFD plants cannot be built near cattle farms. The economics of scale are appealing -- 300 CFD entails an added investment of less than one-half that for 100 CFD. Even the small 100 CFD unit, within the reach of an 'average' farmer, yields enough gas to support a family of 5-6. Furthermore the 15 tons of manure furnishes 225 kg of nitrogen assuming 1.5% N content.

If we assume an average holding of 3 hectares per family (actually 75% of some 500 million holdings are said to be 2 hectares or less), the nitrogen content of the manure represents a seven-fold increase in the present rate of usage of 10 kg/ha. In a narrow sense, the 100 CFD plant is thus capable of making the farmer self-sufficient in these areas.

Efficiency

The idea of processing animal dung to make manure plus fuels is hardly new. Simple as well as complicated devices for producing methane from organic waste have been reported both in the U.S. and in South America. The distinguishing feature of the dung gas technique is its 'ideal' distribution of fuel and fertilizer involving a simple and low cost device.

One might question as to why dung should not be used directly as manure and N source, and secondly the wisdom of disrupting the age-old practice of using dung cakes for cooking and other fuel. (In India 70 million tons of dry dung are used annually for fuel). The rationale lies in improved efficiency and selectivity. For instance, 60% thermal efficiency was reported for gas as opposed to only 11% for dung cakes. Consequently, 20% more useful heat is produced with only 20-25% of dung converted to gas than when the entire dung is burned for fuel. Similarly, it has been claimed that 43% more manure is produced than in manure pit, presumably due to selective decomposition by bacteria in fermentation well.

The availability of fertilizer near the point of application will tend to minimize the considerable costs and losses associated with the distribution of synthetic nutrients. The dung manure is of course not a substitute for ammonia and urea, but will augment them. Even by itself the manure acts as a good soil conditioner, enhancing fertility.

A Plan

We can envision a plan for India for the construction of the capacity to process 100 million tons of dung annually, one-eighth the total production of dung.

The potential values of products of the dung gas system are presented in the following Table. The estimated yield of N nutrient alone amounts to 3.3 million tons - more than sufficient to bridge the gap between India's projected demand and supply through at least 1980. NPK output totals 4 million tons or \$1.5 billion. (If imported, these would have claimed more than one-half of India's foreign exchange earnings from exports). The co-product bio-gas (200 billion CF; 550 Btu/CF) is valuable not only for its \$250 contribution, but in that it will deter diversion of dung to solid fuel usage.

Table 4. Products and Value of 100 Million Tons/yr. Cattle Dung Processed in Dung Gas Units

| <u>Product</u> | <u>Quantity/yr.</u> | <u>Equivalent to</u> | <u>@</u> | <u>Value</u> |
|---|---|--|---------------|-----------------|
| <u>Fertilizer</u> | | | | |
| Nitrogen N | 1.5 MM tons | 3.3 MM tons urea | \$275/mt | \$900 MM |
| Phosphate P ₂ O ₅ | 1.5 MM tons | | \$300/mt | \$450 MM |
| Potash K ₂ O | 1 MM tons | | \$150/mt | \$150 MM |
| <u>Fuel</u> | | | | |
| Dung gas or Bio-gas | 200 billion CF or 11,000 billion Btu | 107 billion CF natural gas, 1,030 Btu/CF | \$2.27/MM Btu | \$250 MM |
| Total | | | | \$1,750 Million |

References

- International Research in Agriculture, Consultative Group in International Agriculture Research (CGIAR), New York, 1974
- "Why Not Kill the Cow?", G.V.Ramakrishna, Embassy of India, Washington, D.C.
- Install a Cow Dung Gas Plant, Ministry of Agriculture and Irrigation, Government of India
- India 1975, Government of India Publications Div., New Delhi, India
- An Appraisal of the Fertilizer Market and Trends in Asia, TVA National Fertilizer Development Center
- United Nations Statistical Yearbook, 1974
- Recent Developments in the Fertilizer Industry, UN Report of Second Interregional Fertilizer Symposium, Kiev and New Dehli, Sept-Oct. 1971
- Reducing Fertilizer Costs, UN Fertilizer Industries Series, Monograph 7; June, 1974
- Nitrogen Fixation Research: A Key to World Food?, R.Hardy and U.Hawelka, Science, May, 1975
- Regional Research Labs, Hyderabad, India, Personal Communication
- Skeist Laboratories, Inc., Internal Data

THE NATURE OF PYROLYTIC OIL DERIVED FROM MUNICIPAL SOLID WASTE.

Kenneth W. Pober, H. Fred Bauer, Occidental Research Corporation,
1855 Carrion Road, La Verne, California 91750.

The Occidental Research Corporation is developing a flash pyrolysis process for the production of fuels and chemicals. The main features of the process are near ambient pressure, no requirement for added chemicals, low capital investment, flexibility of feedstock (municipal refuse, coal, rice hulls, grass, tree bark), variability of temperature, and minimum feed pretreatment. Municipal solid waste is shredded; metals and glass are recovered and sold. The organic fraction, largely cellulose, is pyrolyzed. The resultant pyrolytic oil has a low ash content relative to the feedstock, and the oil can be burned for fuel value. The properties of this oil will be discussed in terms of analyses, viscosity, solubility, thermal stability, corrosion, and char content.

HYDROGEN PRODUCTION FROM BLACK LIQUOR WASTES

by

K.T. Liu, E.P. Stambaugh, H. Nack, and J.H. Oxley

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

INTRODUCTION

In a typical pulping process, approximately one-half of the raw material is converted to pulp and the other half is dissolved in the spent liquor. In the United States, nearly all of the spent liquor is concentrated and burned to provide part of the energy for the plant. One potential method of utilizing these liquors is to produce gaseous products for fuels, chemicals, and other applications. This suggestion is based on the following reasons: (1) the carbonaceous material of black liquor is well dispersed, (2) the black liquor contains considerable amount of alkali metals, which are known to have excellent catalytic effect on gasification, and (3) the concentrated black liquor contains about 40 to 60 percent of water, which can be converted to steam for the carbon-steam gasification reaction.

Because of the presence of carbonaceous material and water in the black liquor, it is suspected that the following water-carbon reactions would predominate:



Normally, the hydrogen concentration in the product gas should not exceed a certain limit imposed by thermodynamic equilibrium. For example, for a typical sodium-base spent liquor, the hydrogen concentration in the pyrolytic gasification products at 1000 K and ambient pressure will not exceed 60 percent in volume (1). However, in the presence of a CO_2 -removal reagent, such as NaOH or CaO, etc., the equilibrium can be shifted

to drive reaction (2) toward completion. This would maximize the hydrogen yield, and, at the same time, reduce CO and CO₂ concentrations in the product gas.

The feasibility of utilizing the spent liquor via pyrolytic gasification at nearly atmospheric pressures has been demonstrated by Prahacs et al^{(1), (2)}. They concluded that the Na-base liquor gave highest yields of hydrogen and carbon monoxide. However, the hydrogen in the product gas was generally in the range of 50-60 percent by volume. The objective of this paper is to demonstrate experimentally the technical feasibility of producing hydrogen-rich gas by pyrolytic gasification of black liquor. Sodium hydroxide was selected as a CO₂-removal reagent for convenience of handling in a microreactor used in this study.

EXPERIMENTAL

The gasification experiments were conducted in a batch reactor system as shown in Figure 1. The reactor was made of a 12-inch-long 3/4-inch Inconel pipe (I.D. 0.742", O.D. 1.050"). Helium was used as an inert tracer to provide a material balance from which gasification yield was estimated.

In a typical experiment, the reactor was brought to the selected reaction temperature, evacuated, and then pressurized to 20 psig with helium. With valves V6 and V7 closed, a measured amount of water (0.5 cc, typically) was loaded into the sample reservoir through V5 by means of a hypodermic syringe and V5 was closed. The free space above the water sample in the reservoir was pressurized to 300 psig with argon (to serve as piston gas) and isolated by closing V4 before the water was forced into the heated reactor by opening valve V6 and immediately closing it. This provided a steam environment for gasification. With the same procedure, a measured amount of black liquor (2.0 cc) was then injected into the steam-filled reactor, except that 600 psig of helium pressure was

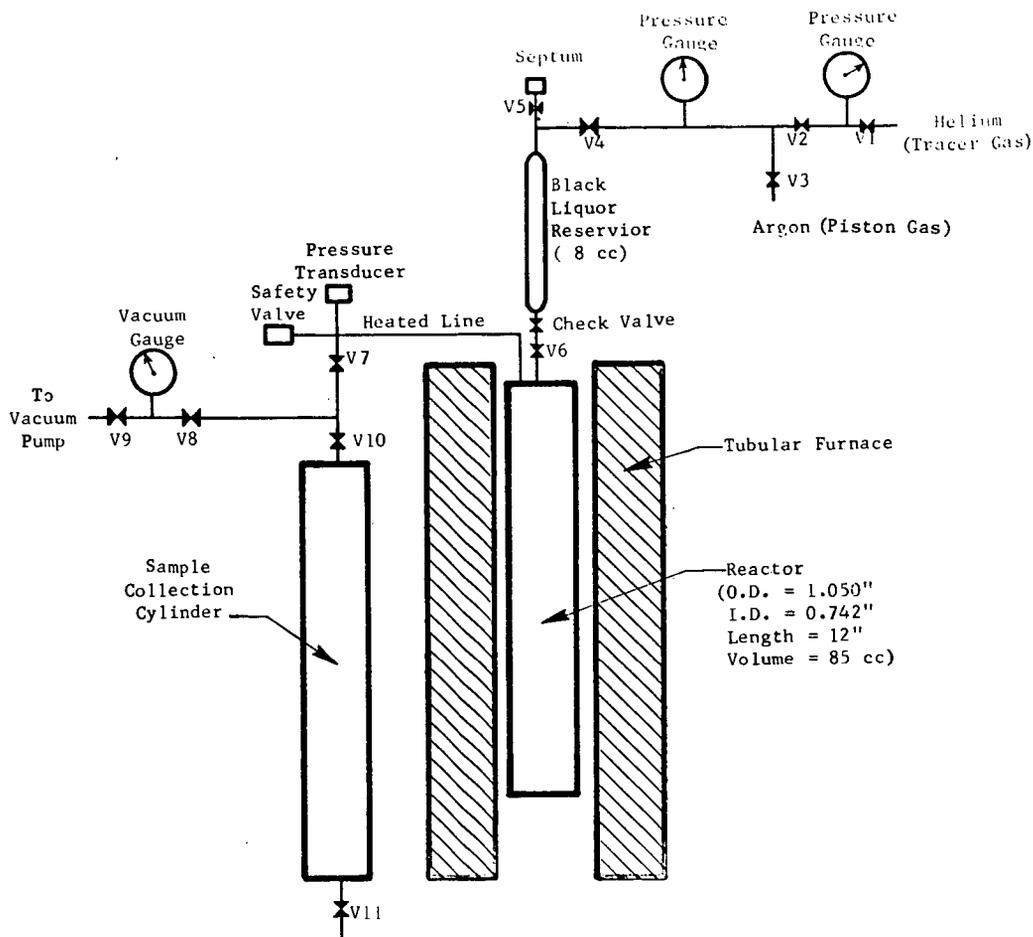


FIGURE 1. EXPERIMENTAL SETUP FOR BLACK LIQUOR GASIFICATION

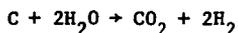
used as a piston gas. Vaporization of the solution took place almost instantaneously. After the predetermined reaction period, the products were collected by opening valves V7 and V10 to transfer the sample to the collection cylinder. The collected gaseous reaction products were analyzed by gas chromatography and mass spectroscopy.

All experimental tests to be discussed in this paper were conducted at 800 C. Two minutes were selected as the reaction time.

The sodium-base black liquor used in this study contained 15.6 percent by weight organic carbon. To investigate the addition of CO₂-removal reagent, various amounts of sodium hydroxide were added to the liquor at Na/C mole ratios of 0.00, 0.38, 0.77, and 1.15, where Na is moles of added sodium and C is moles of organic carbon in the liquor.

RESULTS

The results from the above-mentioned experiments are shown in Table 1 and Figures 2 and 3. The degree of gasification was estimated by assuming that hydrogen and carbon dioxide is produced according to the carbon steam reaction:



Therefore, for every two moles of hydrogen produced, one mole of organic carbon in the black liquor should be gasified. The carbon dioxide thus formed would react with NaOH to form sodium carbonate, up to the limit imposed by the quantity of NaOH added and/or already present in the black liquor. The following observations were made: the main reaction products were found to be hydrogen, methane, carbon dioxide, and carbon monoxide; very small amounts of C₂-C₆ hydrocarbon (rarely exceeding 1.3 percent total) were observed; the concentration of hydrogen in the gaseous products was very high in all experiments, ranging from 62 to 88 volume percent.

TABLE 1. RESULTS OF PYROLYTIC GASIFICATION
OF BLACK LIQUOR

| Run No. | PG-01 | PG-02 | PG-03 | PG-04 |
|--|------------|-------------|-------------|-------------|
| Temp (C) | 800 | 800 | 800 | 800 |
| Na/C Mole Ratio in Feed ⁽¹⁾ | 0.00 | 0.38 | 0.77 | 1.15 |
| Product Yield (g-mole/1000 cc of as-received liquor) | | | | |
| H ₂ | 6.85 | 11.96 | 16.77 | 18.35 |
| CO | 0.45 | 0.36 | 0.40 | 0.12 |
| CH ₄ | 1.88 | 2.70 | 2.01 | 1.90 |
| CO ₂ | 1.69 | 1.30 | 1.00 | 0.42 |
| C ₂ H ₄ | 0.008 | 0.012 | 0.007 | NIL |
| C ₂ H ₆ | 0.039 | 0.087 | 0.012 | 0.051 |
| C ₃ H ₆ | 0.002 | 0.007 | 0.003 | 0.006 |
| C ₃ H ₈ | NIL | 0.005 | NIL | NIL |
| C ₆ H ₆ | 0.005 | 0.12 | 0.077 | 0.08 |
| Product Composition (%) | | | | |
| H ₂ | 62.4 | 72.3 | 82.7 | 87.7 |
| CO | 4.1 | 2.2 | 2.0 | 0.57 |
| CH ₄ | 17.1 | 16.3 | 9.9 | 9.1 |
| CO ₂ | 15.4 | 7.9 | 5.0 | 2.0 |
| C ₂ H ₄ | 0.07 | 0.07 | 0.03 | NIL |
| C ₂ H ₆ | 0.35 | 0.53 | 0.08 | 0.24 |
| C ₃ H ₆ | 0.01 | 0.04 | 0.02 | 0.03 |
| C ₃ H ₈ | NIL | 0.03 | NIL | NIL |
| C ₆ H ₆ | <u>0.6</u> | <u>0.72</u> | <u>0.38</u> | <u>0.38</u> |
| | 100.33 | 100.09 | 100.11 | 100.02 |
| Percent Gasification (based on carbon input) | 40.0 | 64.0 | 72.5 | 75.6 |

(1) Na-content refers to the amount of NaOH added to the liquor.
C-content is 15.6 wt %.

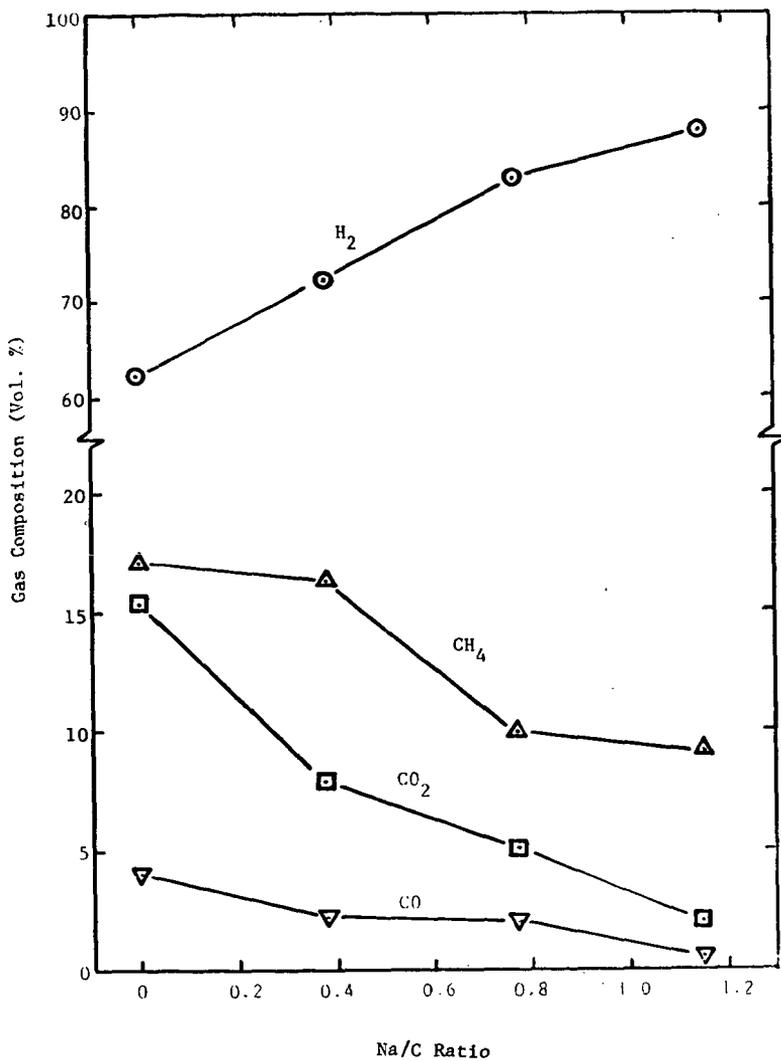


FIGURE 2. PRODUCT GAS COMPOSITION

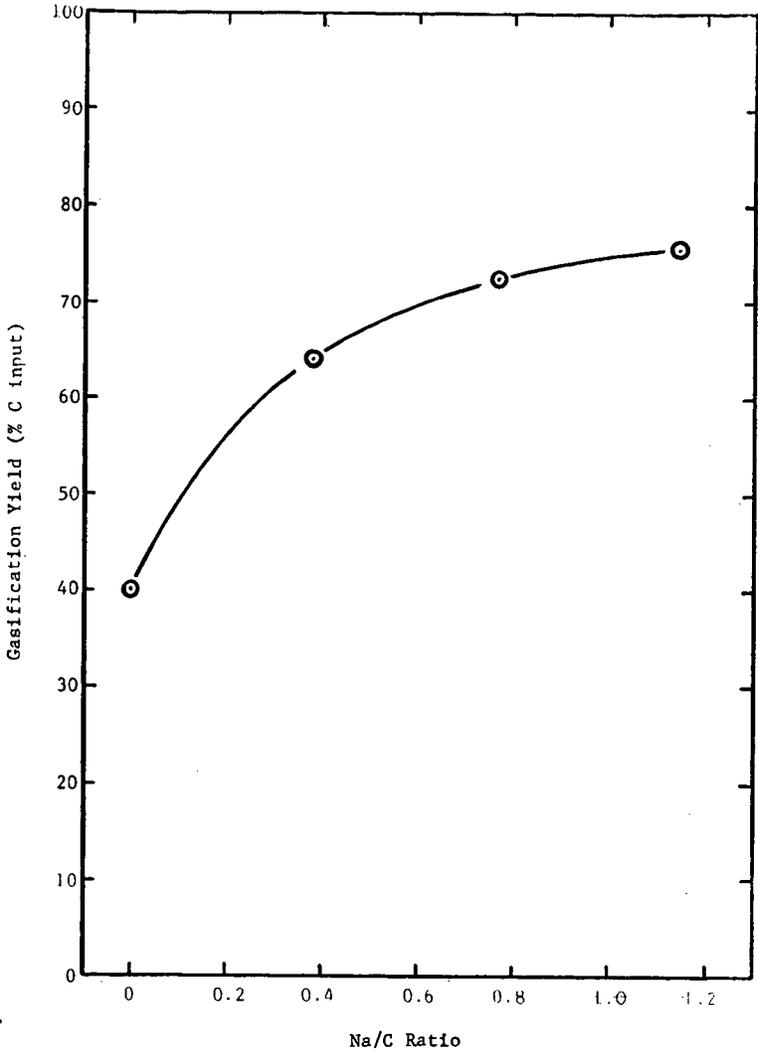


FIGURE 3. GASIFICATION YIELD

There are two striking effects of the added caustic soda on the gasification of black liquor. The first is the product-gas distribution, and the second is the total gasification yield. As shown in Figure 2, the hydrogen content of the gas increased with increasing Na/C ratio; about 88 percent of hydrogen was obtained with Na/C ratio of 1.15 as compared to 62 percent when no free NaOH (Na/C = 0.00) was added to the black liquor. Also, the CO and CH₄ concentrations, in general, decreased progressively with increasing Na/C ratio. The total gasification yield as a function of Na/C ratio is shown in Figure 3. Significant increases in total gasification yield with increasing Na/C ratio were observed. About 76 percent of conversion can be obtained at Na/C of 1.15, as compared to 40 percent, when no free NaOH was added to the black liquor. This suggests that the added alkali metal greatly enhances the gasification reaction.

CONCLUSIONS AND DISCUSSION

In conclusion, the production of hydrogen in concentrations greater than 85 percent in the gas from pyrolytic gasification of black liquor is technically feasible. The addition of caustic soda to the black liquor not only enhances the gasification reaction, but also increases the hydrogen concentration in the product gas. Other reagents, such as calcined limestone or dolomite, may be substituted for the caustic soda.

Thus, a waste material, which presents a disposal problem and a potential pollution hazard, can be converted to products for useful fuels, chemical feedstocks, and/or applications.

LITERATURE CITED

- (1) Prahacs, S. and Gravel, J.J.O., "Gasification of Organic Content of Sodium-Base Spent Pulping Liquors in an Atomized Suspension Technique Reactor", Ind. & Eng. Chem. Proc. Des. & Devel., 6 (2), P 180 (1967).
- (2) Prahacs, S., "Pyrolytic Gasification of Na-, Ca-, and Mg-Base Spent Pulping Liquors in an AST Reactor", Fuel Gasification, Advances in Chemistry Series, Vol. 69, American Chemical Society Publications (1967).

ECONOMIC CONSIDERATION AND ENERGY POTENTIAL OF AGRICULTURAL WASTES

Frederick T. Varani
John J. Burford, Jr.

Bio-Gas of Colorado, Inc., 5620 Kendall Ct., Arvada, Colo. 80002

Introduction

Bio-Gas of Colorado has been doing business as a company for two years dealing with treatment and reuse of agriculture waste organic materials.

We believe a commercially viable energy from the agricultural waste conversion industry potentially exists. This paper attempts to illustrate this statement.

Our research and studies have been conducted in Colorado, Arizona, Utah and New Mexico in conjunction with grants from the 4-Corners Regional Commission. Much of our design information has been accumulated from pilot plant operations and studies at the Monfort of Colorado Inc. beef feedlots. However, the information presented in this paper deals with Colorado exclusively.

Background

Agriculture waste material such as steer manure has an energy value which ranges from 3000-8000 BTU per pound of solid material. This material currently is being used, almost exclusively, in its traditional manner as an addition to agricultural croplands. Various processes, well known and reported, are available to convert this manure into a form of energy product such as oil or gas.

The most often reported processes are:

- 1.) direct combustion
- 2.) pyrolytic conversion
- 3.) anaerobic digestion

Our studies have been exclusively concerned with the process of anaerobic digestion for reasons which will be discussed later.

Definition

First, we'll discuss what we consider would be agricultural wastes of an energy producing nature. Specifically we have defined agriculture wastes as:

- 1.) Residue from animal husbandry operations
- 2.) Food processing wastes
- 3.) Crop residue left in the fields (or collected)

These materials are all generated in large quantities. Items one and two are in a reasonably centralized or collected form and are generated on a continuous basis. Item three is neither generated continuously or normally collected.

In Colorado, crop residues are not removed from the fields and most agriculture state agents strongly recommend leaving this material on the fields for erosion control in the windy climate.

Amounts

Anderson(1) estimates 194.5 million tons of moisture and ash free organic material from animal husbandry operations are generated yearly in the U. S.

Burford (2) estimates that 1,065,500 tons per year of dry organic material (volatile solids) are collectable from 17 areas of concentrated livestock feeding in Colorado. The maximum distance considered for transporting manure was 15 miles. This information was generated during the summer of 1975 and represents approximately 52% utilization of the state feedlot capacity.

In Colorado, 8 areas or potential sites have been located in which the quantity of manure generated is large enough to justify a utility size methane facility.

Available Energy

Before going into the amount of "deliverable" product such manure could generate, a discussion of the conversion process and the state of the "delivered" feedstock is in order.

Manure, as delivered, from an open dirt feedlot (found in Colorado or in the southwest in general) would be extremely variable in a) moisture content, b) dirt or grit ratio and c) extent of decomposition caused by exposure during the confinement period. Figure 1 shows decomposition and organic carbon loss in a typical manure sample versus exposure time. Figure 2 shows a typical steer manure as received per ton breakdown.

As mentioned earlier, our work has been exclusively devoted to the utilization of anaerobic digestion to process the manure. Manure as a "fuel" must be processed before direct combustion or pyrolytic decomposition could be practical. Anaerobic digestion however, would be less affected by moisture content, being a process whereby dilution with water is accomplished before utilization. Dilution allows the grit to be removed by simple sedimentation. The energy loss is less due to the water content than in other mentioned processes.

However, the main reason that digestion is viewed by the authors as the only viable process for utilizing the energy value of the manure is that the process allows the nutrient and humus values of the manure to be available to the farm community. Any process which destroyed nutrient and humus value of manure would be found in much disfavor by the agriculture community.

Anaerobic digestion is a process which utilizes bacteria to decompose (ferment) the organic fraction of the waste material.

The bacterial action is a complex process and a discussion of bacteria fermentation is neither the intent of this paper or practical in the time allowed, however, for those interested, a bibliography of excellent sources for this discussion is included in the reference section of this report. (3, 4, 5, 6)

Basically the following items are of importance in the efficient bacterial decomposition of organic material.

- 1.) Oxygen free environment - Those bacteria known as methanogenic bacteria are strict anaerobes and cease functioning in the presence of oxygen. This requires sealed tankage.
- 2.) Proper digestion time- The bacteria function at a rate proportional to temperature between 60-110°F (15.56-43.33°C) Mesophilic range, and 120-150°F (48.89-65.56°C) Thermophilic range.

At any given temperature enough time (minimum digester tank volume) must be provided to allow the methanogenic bacteria to properly process the organic material. A minimum time of 10 days is required at the Mesophilic temperature of 98°F, and 4.75 ft³ of methane is generated for every pound of organic matter introduced into the system.

- 3.) Temperature uniformity - Although digestion will proceed at any of the temperatures mentioned, temperature changes greater than + 2°F in any 24 hour period are enough to cause "temperature shock", a phenomena whereby the bacteria become relatively dormant and gas production ceases. This requires a temperature control system and insulation of the digestion vessel.
- 4.) Nutritionally balanced feedstock - The bacteria require basically, organic carbon (lignin or non-organic forms of carbon will not digest), nitrogen, phosphorous and trace elements. Manure has enough of all the nutrients required. Increases in organic carbon alone could be tolerated with a resulting increase in gas production.
- 5.) Absence of toxic elements - Heavy metals and ionic material of high concentration can cause bacteria to cease functioning.

When the proper conditions are provided, the bacterial action can take place and the process of degradation or fermentation can take place.

The gas released from the process is known as bio-gas and roughly consists of 50%-70% CH₄, 30% CO₂ and a trace of H₂S by volume.

Our pilot plant consistently produced a gas of 55% CH₄ by volume (at Denver altitude) and verified that 4.75 ft³ of CH₄ could

be generated for every pound of organic matter.*

Process Consideration

Figure 3 shows a basic flow schematic as proposed for the Monfort Gilcrest feedlot. This facility is sized to handle 100,000 cattle units of manure input. (A cattle unit is 1 animal of 1000 lbs weight). Again a complete description of the process (one of many proposed) is beyond the scope of this report but basically, the feed-manure is:

- 1.) mixed with water,
- 2.) sand and grit removed,
- 3.) the resulting slurry is heated and
- 4.) introduced into digestion vessels where digestion occurs.
- 5.) Bio-gas removed, H_2S and CO_2 removed, compressed and sent into the interstate pipeline.
- 6.) Residue removed from digestion vessels, solids separated, remaining liquid is admitted to aeration basin.
- 7.) The liquid is aerated allowing aerobic bacteria to grow.
- 8.) Solids again separated and the remaining liquid remixed with manure.

Plant Performance

A 100,000 cattle unit facility would input 1,200,000 lbs of dry solids per day to the plant. The plant will use 4 digester vessels of 1,000,000 ft^3 capacity each to provide the required detention time for bacterial action. Methane generated would be 3,406,000 ft^3 /day, at a cost of \$1.60 - \$2.00/1000 ft^3 . The bio-gas would be cleaned to the extent necessary and compressed to a pipeline pressure of 850 psig for sale.

Digester Heating

Judicious use of insulation and heat exchange are required in the process to keep the net energy requirements as low as possible. A coal fired boiler will provide a majority of the net digester heating requirement. Augmenting heat sources will be waste heat of compression and solar energy. A form of flat plate collector using digester effluent as the heating medium has been patented and incorporated into the system design.

Capital Costs

Bio-Gas of Colorado has been engineering on this facility for 2 years and our latest capital cost estimate shows a \$5,500,000 - \$6,500,000 cost for this facility. (\$1,610 - \$1,910 capital cost per generated MCF) Figures 4 and 5 show capital cost figures for digestion systems of various sizes as explained on each figure.

* On a theoretical basis the breakdown of 1 lb of cellulose would yield 7 ft^3 of methane. 4.75 ft^3 is an actual yield.

We have built several of the smaller sizes as shown on figure 4, and these figures include 40% markup over cost for the builders.

Figure 5 is estimated and assumes costs as related to an owner-operator, however, IDC and contingency of 15% are allowed in figure 5. As can be seen from 10,000-100,000 cattle units is the least size sensitive area on the curve and 40,000-50,000 cattle units would be required to "make the deal" interesting to anyone contemplating a manure/gas facility.

Some explanation of construction techniques is in order to justify figure 5.

The process flow schematic is relatively simple. The facility consists basically of large tanks and lagoons for holding slurries and allowing anaerobic and aerobic bacteria to process the material feedstock. The physical size of the tanks required to allow the proper hydraulic detention time is the feature which causes the largest increment of capital cost in the envisioned facility. Traditional sewage plant design relies on concrete and/or steel tanks, each custom engineered and field erected.

A factor cost much reported for these municipal installations is \$2.00/ft³ of digester volume.

In the envisioned facility, all tanks including the digester vessels themselves, the clarifiers and lagoons are all "Hypalon-lined" in-the-ground-trenches, a type of construction finding favor in more recent waste treatment projects. Use of this type of construction has allowed keeping the total capital costs under \$2.00/ft³ for this type of facility. This includes the extra equipment such as slurry mixing, gas cleaning and compression, and liquid aeration that a municipal facility would not require.

Conclusions

It is our contention that a potentially viable energy producing industry could be operated in Colorado and in other agriculturally oriented states for the following main reasons:

- 1.) Manure is available in "commercial" quantities in a collected form.
- 2.) Today manure is available at \$2.00/ton or less (\$.615 - \$.705 million BTU). As a fuel manure today is cheaper than coal.
- 3.) The technology is well known to convert the energy value of manure into a very desirable form.
- 4.) It appears the cost of capital for the conversion facility (under \$2,000 per generated MCF) is also desirable.

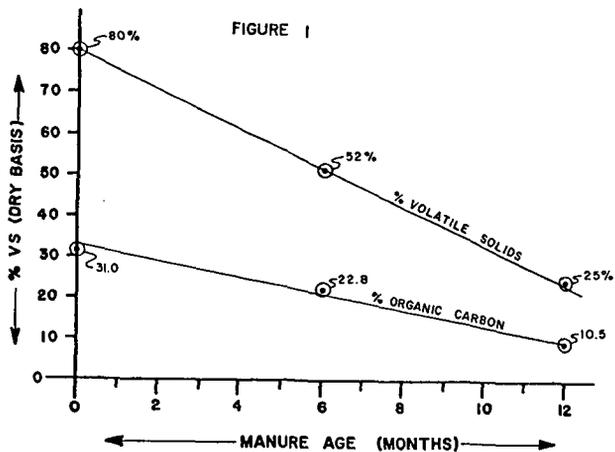
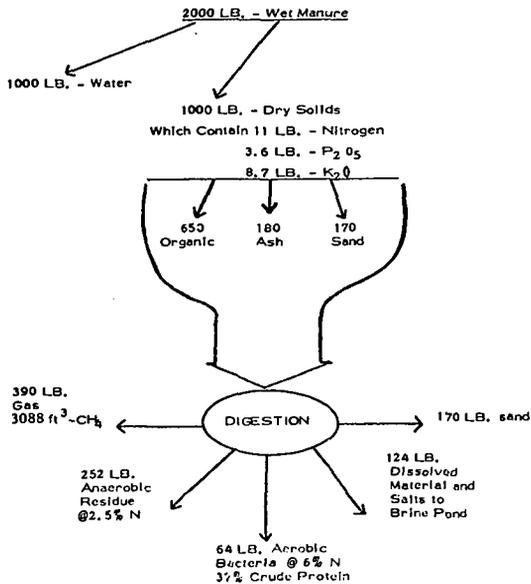


FIGURE 2
PLANT INPUT & OUTPUT
ON UNIT WET TON BASIS

• Expected manure scraped → 4.0 Ton per head per year

• Input - Output:



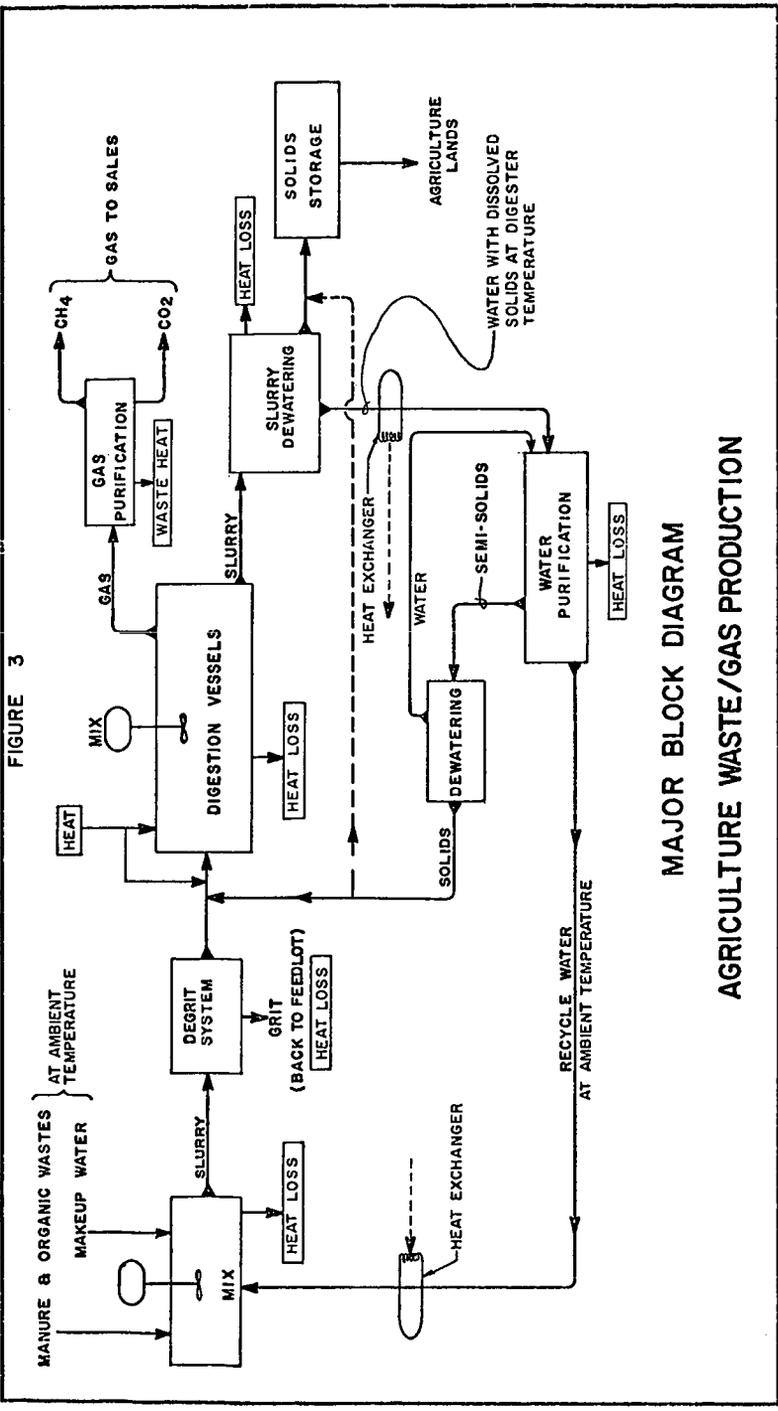


FIGURE 3

FIGURE 4

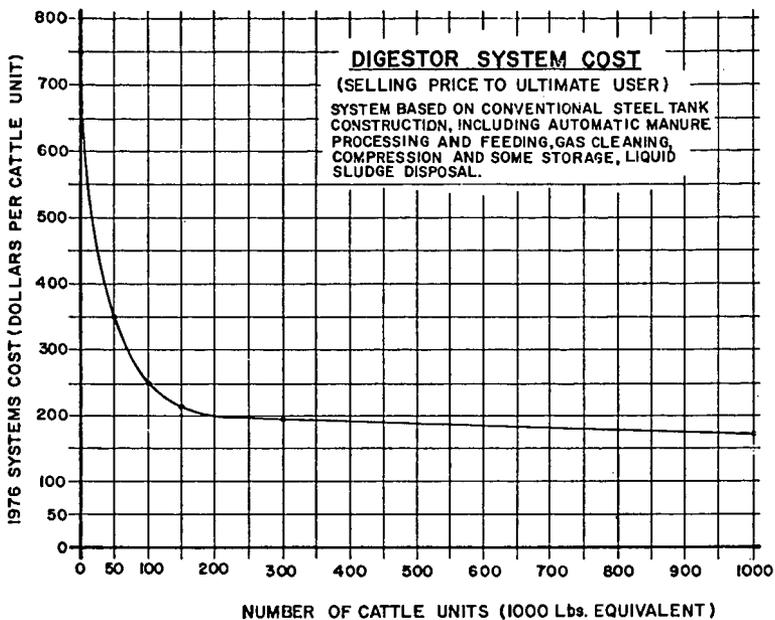
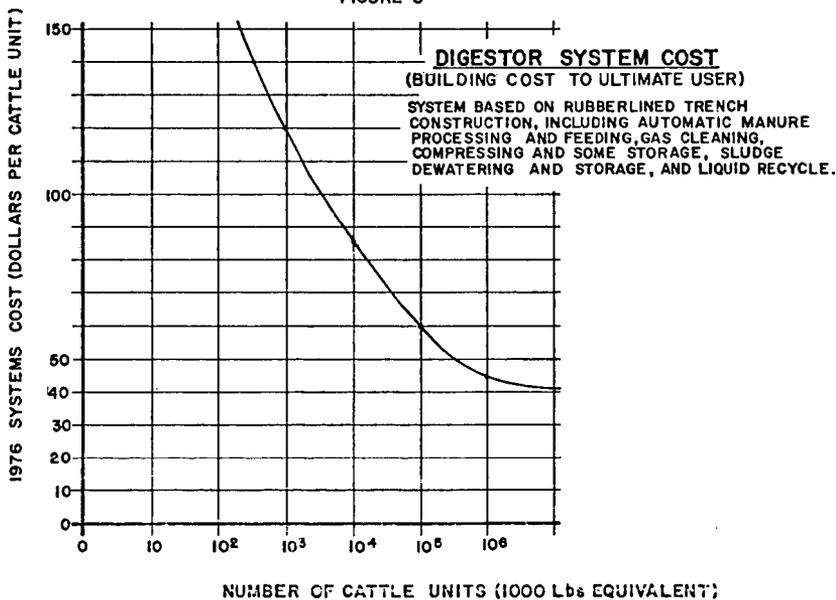


FIGURE 5



REFERENCES

- 1.) Anderson, L. 1972. Energy Potential from Organic Wastes: A Review of the Quantities and Sources. Bureau of Mines, Information Circular 8549, U. S. Dept. of Interior.
- 2.) Burford, J. 1975. Energy Potential Through Bio-Conversion of Agriculture Wastes: 1st Progress Report 4-Corners Regional Commission Grant FCRC No. 651-366-075, 4-Corners-Regional-Commission.
- 3.) Metcalf and Eddy, McGraw Hill Book Company, 1972.
- 4.) Jewell, William J, Energy, Agriculture and Waste Management, Ann Arbor Science Press, 1975.
- 5.) McCarty, P. L. "Anaerobic Waste Treatment Fundamentals: I. Chemistry and Microbiology" Public Works 95,9,107 (1964).
- 6.) Pohland, F. G., and Ghosh, S., "Kinetics of Substrate Assimilation and Product Formation in Anaerobic Digestion" Journal WPCF, Vol. 46, No. 4, April, 1974.

PIPELINE GAS FROM SOLID WASTES BY THE SYNGAS RECYCLING PROCESS. H. F. Feldmann, G. W. Felton, H. Nack, Battelle, Columbus Laboratories, 505 King Avenue, Columbus, Ohio, 43201; J. Adlerstein, Syngas Recycling Corp., Suite 2120, The Thomson Building, 65 Queen Street W., Toronto, Ontario, Canada M5H 2M5

A two-stage process for converting solid wastes into a methane rich gas capable of being upgraded to pipeline quality is described. In the first zone, the raw solid wastes are contacted with a hydrogen containing gas and are converted to hydrocarbon gases consisting mostly of methane with smaller amounts of ethane, carbon oxides, carbonaceous char and less than one percent oil. The char is used in a second stage connected reactor to generate a synthesis gas for the first stage. Results of continuous operation of the first stage as both a moving-bed and free-fall reactor are presented and these data are combined with gasifier performance calculations to establish large-scale performance characteristics of the integrated system.

THE GASIFICATION OF WASTES USING MOLTEN SALTS

S. J. Yosim and K. M. Barclay

Atomics International Division

8900 De Soto Avenue

Canoga Park, California 91304

INTRODUCTION

This paper describes some experimental results showing the technical feasibility of producing a low Btu gas (100-150 Btu/scf) from wastes using molten salt technology. The concept of molten salt gasification is described first and is followed by a description of the experimental apparatus. Then some results of bench scale gasification tests of selected wastes are given.

The disposal of waste x-ray film is discussed. While low Btu gas can be produced with film, a more important objective is to recover the silver from the film. Therefore, experiments to recover silver as well as experiments producing low Btu gas are described.

The discussion of film tests is followed by tests in which rubber tires and paper are gasified.

Then, some tests on the disposal of nitropropane are described. Organic NO_2 -containing compounds can be present in other wastes and, since they are a source of nitrogen oxides emissions due to their high nitrogen content, tests were carried out to determine if such wastes could be disposed of with low NO_x emissions.

The experimental portion of the paper concludes with a description of some gasification tests with sugar. Sugar was tested because it is a well-characterized oxygen containing substance and has a composition typical of many solid wastes.

A discussion of the results, including a comparison of these results with those of coal and oil gasification using the same technology, concludes the paper.

CONCEPT OF GASIFICATION OF WASTES WITH MOLTEN SALT

Molten Salt Gasification of wastes is a process which provides for the removal of pollutants during an initial partial oxidation and gasification step followed by complete burning of the clean combustible gases in a secondary combustor. Thus, the Molten Salt Gasification Process for the disposal of wastes is a two-step process.

In the first step, shredded combustible waste and air are continuously introduced beneath the surface of a sodium carbonate-containing melt at about $1,000^{\circ}\text{C}$. The waste is added in such a manner that any gas formed during combustion is forced to pass through the melt. Any acidic gases, such as HCl (produced from chlorinated organic compounds) and H_2S (from organic sulfur compounds) are neutralized and absorbed by the alkaline Na_2CO_3 . The ash introduced with the combustible waste is also retained in the melt. Any char from the fixed carbon is completely oxidized in the salt. The temperatures of gasification are too low to permit a significant amount of NO_x to be formed by fixation of the nitrogen in the air. Gasification of the waste is accomplished by using deficient air, i.e., less than the amount of air required to oxidize the waste completely to CO_2 and H_2O . Thus, in the first step, the waste is partially oxidized and completely gasified in the molten salt furnace. The gas generated has an effective heating value which depends upon the original waste. Values of approximately 150 Btu/scf have been obtained.

In the second step, this gas flows to a conventional gas-fired boiler in which it is combusted with secondary air, producing steam.

As a possible option, a sidestream of sodium carbonate melt can be withdrawn continuously from the molten salt furnace, quenched and processed

in an aqueous regeneration system which removes the ash and inorganic combustion products retained in the melt and returns the regenerated sodium carbonate to the molten salt furnace. The ash must be removed to preserve the fluidity of the melt at an ash concentration of about 20 weight %. The inorganic combustion products must be removed at some point to prevent complete conversion of the melt to the salts, with an eventual loss of the acid pollutant-removal capability.

This concept is the basis of the Molten Salt Coal Gasification Process which is currently being developed by Atomics International.

In the molten salt concept for silver recovery, the film is gasified in a Na_2CO_3 melt in the same manner as other combustible waste. The silver from the film forms a liquid metal pool which is drained from the bottom of the combustor to form metal ingots with a purity exceeding 99.9%.

EXPERIMENTAL

Materials

The waste x-ray film was analyzed and was found to contain in weight %: carbon, 53.2; hydrogen, 5.5; ash (which was essentially silver), 2.4; and the oxygen (by difference), 38.9. Direct analysis for silver showed that the film contained 2.3% silver. The wood was pine sawdust with a moisture content of 2.8%. No chemical analyses were carried out, but a typical composition for pine wood on a dry basis is: carbon, 51.8; hydrogen, 6.3; ash, 0.5; and oxygen, 41.3. The heating value is typically 9,130 Btu. The rubber was buffings from an automobile tire tread. No chemical analyses were carried out. The nitropropane was practical grade obtained from Eastman. The sugar consisted of pure sucrose. The Na_2CO_3 for the salt bath was technical grade material obtained from Kerr McGee.

Bench-Scale Molten Salt Gasifier

A cross-section view of the bench-scale molten salt gasifier is shown in Figure 1. Approximately 12 lb of molten salt are contained in a 6-in. ID

and 30-in. high alumina tube placed in a Type 321 stainless steel retainer vessel. This stainless steel vessel, in turn, is contained in an 8-in. ID, four-heating zone Marshall furnace. The four heating zones are each 8 in. in height, and the temperature of each zone is controlled by an SCR controller. Furnace and reactor temperatures are recorded by a 12-point Barber-Colman chart recorder.

Solids, pulverized when necessary in a No. 4 Wiley mill to <1 mm in particle size, are metered into the 1/2-in. OD central tube of the injector by a screw feeder. Rotation of the screw feeder is provided by a 0 to 400 rpm Eberback Corporation Con-Torque stirrer motor. In the injector the solids are mixed with the air being used for gasification, and this solids-air mixture passes downward through the center tube of the injector and emerges into the 1-1/2-in. ID alumina feed tube. This alumina feed tube is adjusted so that its tip is $\sim 1/2$ in. above the bottom of the 6-in. diameter alumina reactor tube. Thus, the solids-air mixture is forced to pass downward through the feed tube, outward at its bottom end, and then upward through ~ 6 in. of salt in the annulus between the 1-1/2-in. and the 6-in. alumina tubes. In the case of liquids, a different feed system is used. The liquid is pumped with a laboratory pump and is sprayed into the alumina feed tube.

In order to prevent the melt temperature from rising when an excessive amount of heat is released to the melt, a cooling system (not shown in Figure 1) cooled by air, maintained a constant temperature. It consists of an eight-hole air distribution ring, mounted underneath the stainless steel ceramic tube retainer vessel. Air at rates up to 18 cfm can be passed upward between the outer surface of the retainer vessel and the furnace wall.

Off Gas Analyses

Samples of the exit gas, for analysis by gas chromatography, are taken with 1-ml gastight syringes downstream of the CO_2 analyzer. Two gas samples

are taken at the same time. One sample is analyzed for carbon monoxide, oxygen, and nitrogen, using a molecular sieve 13X column at room temperature. The other sample is analyzed for carbon dioxide, methane, ethane, ethylene, sulfur dioxide, and hydrogen sulfide, using a Poropak Q column at 130°C (266°F). Often, continuous measurements of NO_x, CO, and CO₂, are taken of the off-gas. The NO_x analyses are made with a Thermo Electron Corporation Chemiluminescent NO_x Analyzer. The carbon monoxide and carbon dioxide determinations are made with Olson-Horiba, Inc. units. (Mexa-300 carbon monoxide and Mexa-200 carbon dioxide analyzers, respectively.) All gas analysis data are reported on a dry basis.

Results

The gasification steady state results for film, wood, rubber, and nitropropane are shown in Table 1. The results for sucrose are shown in Table 2.

Film

Two series of tests were carried out with waste x-ray film. The purpose of the first test (No. 1) was to show that pure elemental silver could indeed be recovered under gasification conditions attainable in the Atomics International pilot plant which is capable of gasifying about 200 lbs/hr of coal and waste. A combustible gas with a higher heating value (HHV) of 100 Btu/scf was obtained. In this bench scale test, 15 lbs of film were burned. After the test, the melt was cooled until the silver solidified (960°C). A bright pellet of lustrous silver metal having a weight of 0.34 lbs was recovered. This corresponds to 98.6% of the silver in the film feed. Because of the successful results of this bench scale tests, a test to recover film from 20,000 lbs of waste x-ray film is planned for the near future. (A silver recovery test in the Atomics International's pilot plant has been carried out in which 15,000 lbs of waste x-ray film were burned under excess air conditions at a rate of 100 lbs/hr. In that test, which was carried out for the Navy, a single silver metal ingot weighing 230 lbs with 99.9% purity was recovered.)

In test No. 2, the gasification was carried out under more reducing conditions (22% theoretical air). This time a gas with a much higher heat content was obtained (179 Btu/scf). Elemental silver was recovered from this test also but the yield was not determined.

Wood

Gasification of the pine wood was carried out with 30% theoretical air. Again, a gas with a high heat content (181 Btu/scf) was obtained. The H_2 content was somewhat higher and the CH_4 content somewhat lower than was obtained with the film at 22% theoretical air. However, it is not clear whether this difference is real.

Rubber

Two tests were carried out with rubber from a rubber tire. Since the tire contained organic sulfur which would form Na_2S in the melt, the Na_2CO_3 melt originally contained 6 wt % Na_2S to simulate steady state conditions. Sodium sulfide was also added because it has been established at Atomic International and other laboratories that Na_2S is a catalyst in accelerating the gasification of char in molten Na_2CO_3 . The gasification was carried out with 33% theoretical air. The results in Table 1 are an average of the two tests. A gas with an HHV of 156 Btu/scf was obtained. The CO_2 content of this gas was considerably lower than that from the oxygen-containing wastes and is more similar to that obtained when coal or oil is gasified. In spite of the large amounts of Na_2S in the melt, no H_2S or other sulfur-containing gases (<30 ppm) were detected in the off gas.

Nitropropane

Organic NO_2 -containing compounds may well be present in small amounts in wastes which are being gasified for producing fuel. This type of compound

can emit a great deal of NO_x . In these tests, nitropropane was used to determine if it would be possible to minimize the NO_x emissions during gasification. A series of tests was run under varying conditions and with different additives. It was determined that under certain process conditions and with a specific additive, it was possible to combust nitropropane and produce a product gas containing only 6 ppm NO_x . It thus appears that the presence of organic NO_2 -containing wastes will not contribute much NO_x under gasifying conditions. The composition of a typical off gas from the tests is shown in Table 1.

Sucrose

The gasification of sucrose in pure Na_2CO_3 was studied at four different stoichiometries. The melt temperature was about 950°C . The air feed rate (2.5 scfm) corresponded to an air superficial velocity in the gasifier of 1 ft/sec. As expected, the heating value of the gas increased as the percent theoretical air decreased. However, when the air/fuel ratio was too low, insufficient heat was released to the melt and auxiliary heating was required. This was the case with the test in which 18% theoretical air was used. The furnace was turned on during the test to maintain the melt temperature. However, at 35 and 52% theoretical air, sufficient heat was released to the melt so that the furnace could be turned off. At 72% air, excess heat was generated and had to be removed by the cooler. The relatively short experimental runs (~1 hour) did not permit a definite conclusion as to what minimum percent of theoretical air could be used in this system and still maintain melt temperature without auxiliary (furnace) heat. It appears, however, that the salt could be maintained in a molten state at least at 35% of theoretical air at which level a combustible gas with an HHV of 154 Btu/scf was being generated.

A test in which the air superficial velocity was reduced to 1/2 ft/sec yielded an off-gas virtually unchanged in composition to that when the velocity was 1 ft/sec. This suggests that residence time in the melt is not an important factor.

Discussion

It is of interest to compare the heating value of a gas produced from a material containing a great deal of combined oxygen with that produced from a conventional fuel such as coal and fuel oil. A comparison of the heating values of gases produced by the oxygenated compounds which contain 40-50 wt % oxygen, by Kentucky No. 9 coal (7 wt % oxygen), and by No. 6 fuel oil (essentially no oxygen) using the same molten salt technology is shown in Table 3. It can be seen that the difference in heating value of the gas is relatively small in spite of the large difference in Btu content of the combustible material (12,000 Btu/lb for the coal and 19,000 Btu/lb for the fuel oil vs 7,000-9,000 Btu/lb for the oxygenated material). The small difference in heat content of the gases probably is due in part to the fact that a great deal of the oxygen is supplied by the fuel and this combined oxygen is not diluted with atmospheric nitrogen. To illustrate, the nitrogen contents of the off gas were 59% in the case of fuel oil at 20% theoretical air and only 34% in the case of sucrose at 18% theoretical air.

It has been shown that, as expected, the Btu content of the off-gas increases as the percent of theoretical air decreases. However, as was also shown (in test No. 6), there is a practical upper limit on the gas heat content which can be obtained. Above this upper limit, there will not be enough heat released to the melt to sustain the operating temperature. This upper limit can be increased somewhat by using preheated process air and by decreasing the heat losses in the gasifier with improved insulation.

The maximum waste throughput is also governed by the maximum superficial velocity of the gas through the melt. In general, the maximum superficial velocity of the inlet air has been set at 2 ft/sec. (This corresponds to a somewhat higher velocity of the product gas, depending on the fraction of total oxygen which is combined oxygen and on the composition of the off-gas.) Beyond this velocity of 2 ft/sec, entrainment of the melt becomes excessive. However, by operating at elevated pressures, the waste throughput can be significantly increased since at a given air superficial velocity, the waste throughput will be proportional to the pressure.

No sulfur-containing pollutants were observed in the off-gas when rubber was gasified. While chlorine-containing material was not gasified, in all tests in which that type of material was treated in Na_2CO_3 melts with excess air, there was no trace of HCl even when the Na_2CO_3 content was as low as 5 wt %. It is expected that the same results would be obtained if deficient air were used.

The results described in this paper show that the gasification of wastes in molten salts to produce a low Btu gas is technically feasible. However, an engineering evaluation leading to the economics of molten salt gasification of the various wastes has not been done and would be necessary before it can be established if this process is a practical one.

TABLE 1

Gasification of Wastes

| Test # | Waste | Temp. (°C) | Air Feed Rate (scfm) | Fuel Feed Rate (lb/hr) | % Theor.(a) Air | Composition of Off-Gas (vol.%) | | | | Higher Heating (b) Value (Btu/scf) | |
|--------|--------------|---------------|-------------------------------|---------------------------------|-----------------------|-----------------------------------|------|----------------|-------------------|---|----------------|
| | | | | | | CO ₂ | CO | H ₂ | CH ₄ | | C ₂ |
| 1 | Film | 1015 | 4.50 | 5.34 | 51 | 16.5 | 12.0 | 11.7 | 2.6 | 0.2 | 107 |
| 2 | Film | 958 | 2.50 | 6.58 | 22 | 16.0 | 18.3 | 14.1 | 5.2 | 1.2 | 179 |
| 3 | Wood | 951 | 1.00 | 2.08 | 30 | 14.5 | 20.3 | 21.1 | 3.0 | 0.9 | 181 |
| 4 | Rubber | 920 | 1.63 | 1.81 | 33 | 4.0 | 18.4 | 16.0 | 2.4 | 1.1 | 156 |
| 5 | Nitropropane | 1000 | 2.50 | 2.58 | 75 | 11 | 8 | 9 | NM ^(c) | NM ^(c) | >55 |

(a) Percent of air required to oxidize material completely to CO₂ and H₂O

(b) Calculated from composition of off-gas

(c) Not measured

TABLE 2

Gasification of Sucrose in 100% Na_2CO_3 (a)

| Test # | Solid Feed Rate (lb/hr) | % Theor. Air (b) | Composition of Off-Gas (vol. %) | | | | | Higher Heating Value Btu/scf (c) | |
|--------|-------------------------|------------------|---------------------------------|---------------|------|--------------|---------------|----------------------------------|--------------|
| | | | N_2 | CO_2 | CO | H_2 | CH_4 | | C_2 |
| 6 | 12.2 | 18.4 | 34.3 | 13.5 | 26.9 | 18.9 | 4.3 | 1.9 | 216 |
| 7 | 6.5 | 34.8 | 46.2 | 15.0 | 18.3 | 17.0 | 2.5 | 0.8 | 154 |
| 8 | 4.3 | 52.2 | 57.0 | 19.1 | 12.3 | 9.7 | 1.4 | 0.3 | 91 |
| 9 | 3.1 | 72.1 | 69.8 | 20.0 | 5.5 | 3.1 | 0.7 | 0.1 | 37 |

(a) The melt temperature was 950-960°C. The air feed rate was 2.5 scfm

(b) Percent of air required to oxidize material completely to CO_2 and H_2O

(c) Calculated from composition of off-gas

TABLE 3
A Comparison of the Heating Value of Gas
Produced from Sucrose and from Coal

| OXYGENATED MATERIAL | | | CONVENTIONAL FUELS | | |
|---------------------|-----------------|----------------|-----------------------|-----------------|----------------|
| Material | % Theor. Air | HHV Btu/scf | Fuel | % Theor. Air | HHV Btu/scf |
| Sucrose | 18 | 216 | Fuel Oil ^a | 20 | 191 |
| Film | 22 | 179 | Fuel Oil | 27 | 155 |
| Wood | 30 | 181 | Coal ^b | 35 | 151 |
| Sucrose | 35 | 154 | Coal | 40 | 138 |
| Film | 51 | 107 | Coal | 50 | 118 |
| Sucrose | 53 | 91 | Coal | 70 | 36 |
| Sucrose | 72 | 37 | | | |

(a) The fuel oil was a No. 6 oil. It was API gravity 18, carbon residue, 5%; ash, 0.007%; sulfur, 0.3%, hydrogen 13%.

(b) The coal was Kentucky No. 9 seam coal. The proximate analysis on a dry basis was in weight %; ash, 16.4; volatile matter, 37.6; fixed carbon, 46.0; and sulfur, 4.5. The ultimate analysis on a dry basis was: carbon, 66.3; hydrogen, 4.6; nitrogen, 1.4; sulfur, 4.5; ash, 16.4; and oxygen (by difference), 6.9.

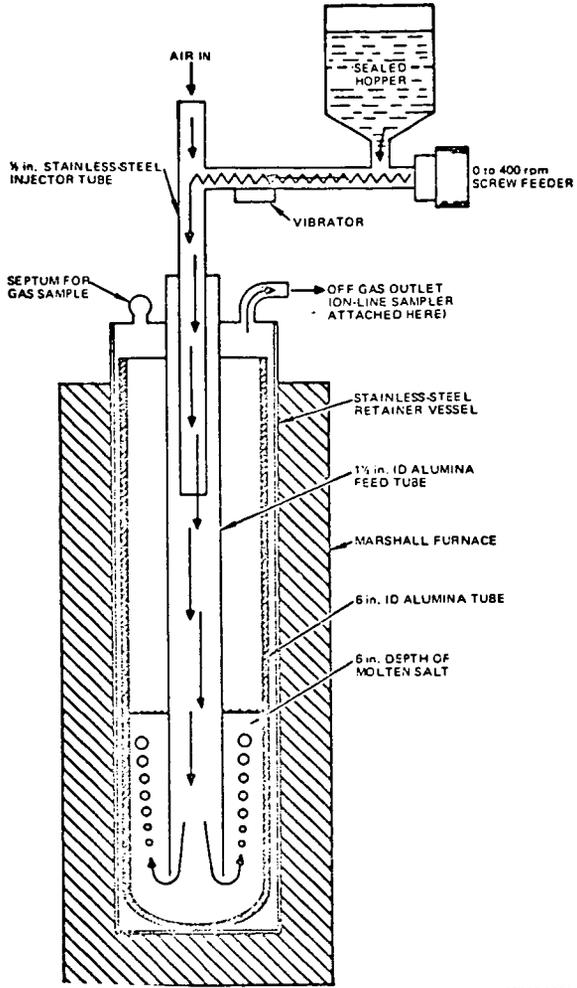


Figure 1. Bench Scale Molten Salt Gasifier Schematic

FUELS FROM WASTES - AN OVERVIEW. Bernard D. Blaustein, Pittsburgh Energy Research Center, U. S. Energy Research and Development Administration, 4800 Forbes Avenue, Pittsburgh, Pa. 15213.

Organic wastes generated in this country are estimated to exceed 800 million tons (on a dry basis) each year. This large and continually renewable energy source is beginning to be used to a significant extent. Solid, liquid and gaseous fuels with different characteristics and markets are being produced. Numerous processes for the recovery of fuels and energy from waste materials are in various stages of research, development, demonstration and commercialization. This paper will discuss these processes and fuels in order to provide an overview of this field of energy technology.