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EFFECT OF STEAM ON H_2, CO_2, H_2S, AND COS CONCENTRATIONS IN COMBUSTION-RETORT OFFGAS

A. K. Burnham

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Lawrence
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Laboratory

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A. K. Burnham
Lawrence Livermore National Laboratory

ABSTRACT

The effect of steam on the offgas composition of combustion retorts was determined by interrupting the otherwise continuous steam flow in S-24 for one hour while other variables, including temperature, remained relatively constant. The offgas composition was determined by frequent gas analyses. The largest effect of interrupting the steam flow was to decrease the rate of H_2 production by a factor of 2.6, primarily due to elimination of the H_2O-char reaction. The rate of CO_2 production decreased by a factor of 1.7. After subtracting the CO_2 production due to carbon combustion, this result implies that steam accelerates the rate of carbonate decomposition by a factor of 3.0. In the absence of steam, the H_2S production rate dropped by a factor of 1.5, indicating the importance of steam-iron sulfide reactions. Finally, the production rates of CO and COS increased by factors of 1.5 and 1.7. These results are compared to results from laboratory studies of oil shale chemistry and to gas production during other parts of this and other LLNL pilot retort runs. Finally, the ability of steam to significantly decrease the pour point of shale oil from combustion retorts is noted.

INTRODUCTION

A number of reports recently have demonstrated the effect of steam on offgas from oil shale combustion retorts[1,2] and on the rates of individual chemical reactions.[3,6] The most pronounced effects have been reported for H_2 production due to steam gasification,[3,4] CO_2 production due to acceleration of carbonate decomposition and/or reaction,[5] and H_2S production due to iron sulfide reactions.[6] Unfortunately, there are often limitations on how much information can be obtained about the net effect on retort offgas from laboratory studies of individual reactions, and vice versa, because of the many interactions between various reactions in a retort. As a guide in understanding the relationship laboratory-scale and pilot-retort-scale results on the effect of steam on combustion retorting of Colorado oil shale, the flow of steam to LLNL retort run S-24 was interrupted for one hour. The results of this experiment provide convincing proof of the effects of steam on pilot retort offgas predicted from laboratory experiments. The increase in H_2 with steam has been noted before, but the expected increase in H_2S and the acceleration of carbonate decomposition had not been confirmed by retort data until now.

Also demonstrated is a decrease in COS concentration in the offgas and the pour point of the oil with steam not previously predicted.

EXPERIMENTAL

Essentially all of the data reported here comes from the LLNL 0.3 x 1.5 m (S) and 1 x 6 m (L) fixed-bed retorts. Most runs used shale from the Anvil Points Mine. It had a typical grade of about 100 ℓ/Mg (24 gal/ton). Four runs (S-20, S-22, L-3, and L-4) used shale from a Rio Blanco mine shaft at Tract C-a.

The effect of steam interruption on offgas composition was determined during retort run S-24. This run used Anvil Points shale with a median particle size of 1.4 cm (-7.6 +0.001 cm) and a grade of 88 ℓ/Mg. The gas inlet flow rates are summarized in Table 1. The average rate of retort front advancement during the middle part of the run was approximately 0.25 m/day. During a one hour period, the steam flow was interrupted while the air continued at a constant rate. All condensers were drained immediately before the interruption to minimize exchange between the gas stream and condensed liquids.

Offgas compositions were determined by a quadruple mass spectrometer (H_2S, N_2, H_2, CO_2, CH_4), gas chromatographs with a flame ionization detector (C_1-C_9 hydrocarbons) and a thermal conductivity detector (CH_4, N_2, CO, CO_2, H_2), and a microwave spectrometer (COS). CO and CO_2 concentrations were also determined by on-line infrared meters.

RESULTS

The change in gas composition due to the interruption of steam flow for one hour is shown in Figure 1. All species except CO were determined at one minute intervals by mass spectroscopy. CO was determined at 5 minute intervals by gas chromatography. There is about a 15 minute delay between the change in the inlet gas composition and the observed change in the exit gas composition. When the steam was shut off, it took about 10 minutes for the inlet flow of air to sweep the 45ℓ void volume in the retort. Another 10 to 15 minutes is required for the exit flow to travel through the condensing system. (The small bumps and dips in gas concentration observed over the time interval when the inlet gas change was detected is related to the fact that the flow rate changes instantaneously with a change in the inlet flow, but the change in composition occurs over a 10 minute period.)

The property most pertinent to discussion of reaction rates is not gas composition, but gas production rate. Because the inlet flow of N_2 was maintained at a constant value, the rate of production of any gas is easily calculated by multiplying the volume ratio of the gas to nitrogen times the nitrogen flow rate. An example of the change in production rate is given in Figure 2 for H_2S. It is easily seen that rate of H_2S production had dropped by about a factor of 1.5 between 51.0 and 52.1 hours into the experiment due to the interruption of steam flow. The change in production rate of other gas species over this time interval are given in Table 2.

Another important parameter is the relative rate of H_2S and oil generation. Campbell[7] has shown that C_3 hydrocarbon evolution closely follows oil evolution, so we use the H_2S/C_3H_x ratio to determine the relative rates of H_2S and oil production. From Figure 3, it is seen that this ratio decreases by a factor of 1.2 when the steam is turned off.

Finally, additional information concerning the importance of various reactions can be obtained from the changes in gas composition during the parts of the retort run. Figures 4 and 5 show the concentrations of C_3H_8, H_2, H_2S, CO, CO_2 and COS during the entire run. Very little H_2S was observed in the offgas until after the steam front reached the bottom of the retort at about 17 hours into the experiment.

DISCUSSION

Steam diluent in a combustion retort acts both as a chemical reactant and a heat carrier.[2] The thermal profile has a somewhat different shape when steam is used. In the steam-interruption experiment during run S-24, the primary effects observed are chemical. The peak temperature in the retort remained constant at 740°C, within 2°C. The heating rate in the kerogen pyrolysis region, as measured by the ethene/ethane ratio, dropped only slightly.[7] The rate of oil generation, as measured by the C_3H_x/N_2 ratio, dropped about 20%.

The largest chemical effect observed was the drop in the H_2 production rate by a factor of 2.6. This is primarily due to the elimination of the steam-char reaction. This effect has been noted earlier by a comparison of similar retort runs with and without steam. In fact, Raley et al[1] indicated a 2.7-fold increase in hydrogen production between runs S-11 and S-13, which differed only by the presence of steam in S-13. Comparison of the hydrogen production in S-13 with that in S-17 (air/N_2 inlet) indicates an increase in H_2 by a factor of 2.1 with steam.

The next largest effect was the decrease in CO_2 production by a factor of 1.7. However, the CO_2 production from combustion remains constant (as long as a negligible or constant amount of O_2 is consumed by oil combustion), so the effect of steam on carbonate decomposition must be larger. If combustion of char (and gas) produces 90% CO_2 and 10% water, it follows that the rate of carbonate decomposition decreased by a factor of 3.0. An effect of this magnitude had been predicted from laboratory kinetic studies,[5] but had not yet been demonstrated in a pilot retort. Usually the temperature in the pilot retorts is sufficiently high to decompose essentially all the carbonate, and the remaining carbonates are concentrated in the interior of larger particles where they are insulated from the gas stream so that steam cannot diffuse in to affect the decomposition rate.

The accelerating effect of steam on carbonate decomposition is confirmed by an examination of the composition of the spent shale in the lower part of the retort. Figure 6 compares the experimental extent of carbonate decomposition with that calculated from the experimental thermal histories using Campbell's non-steam kinetics[8] and assuming a 0.5 atm CO_2 partial pressure in the calcite decomposition expression. There are ten levels in the retort separated by six-inch intervals. In levels 7 through 10, the bottom 30% of the retort, there has been 2.6 times more carbonate decomposition in the shale than calculated. The discrepancy is even larger considering that the temperature of the large particles is undoubtedly somewhat lower than measured by the bed thermocouples.

The next largest decrease was the factor of 1.5 in the H_2S production rate when the steam was interrupted. Laboratory studies had indicated that the steam-pyrite and steam-pyrrhotite reactions in oil shale occur rapidly at 500°C, but thermodynamic calculations based on previous offgas data indicated that the steam-pyrrhotite rate would be severely limited by reaching equilibrium with only very small extent of reaction. The 50% increase in H_2S generation is about the right amount to account for the decreased sulfur residue left in the spent shale (50% in this experiment compared to 65% under assay conditions). This corresponds roughly to complete conversion of pyrite to pyrrhotite in the presence of steam. These values are approximate because the fraction of raw-shale sulfur contained in pyrite varies from 0.7 to 0.9.[9,10]

A similar conclusion can be obtained by examination of elemental analyses reported for LLNL retort runs S-10 through S-23.[2,11] The average distribution of sulfur in products is compared in Table 3 for runs with and without steam. H_2S production is determined by difference because few, if any, of the retort runs had accurate H_2S concentrations measured. The sulfur measurements on liquid and solid products are quite accurate by comparison. We have neglected the fact that approximately 5% of the gaseous sulfur is in non-H_2S compounds and that some of the H_2S dissolves in the retort water as ammonium hydrogen sulfide. The H_2S data in Table 3 indicates a 40% increase in H_2S production with steam, which is in-between the 30% and 50% increases predicted from the H_2S/C_3H_x and H_2S/N_2 ratios during the steam interruption in S-24.

Further understanding of the steam-iron sulfide reactions can be obtained by examining the offgas concentrations after 60 hours into the experiment (shown in Figure 4). The large peak in C_3H_8, H_2 and H_2S concentrations at 78 hours is caused by levels 6 through 10 passing through the kerogen pyrolysis temperature zone at approximately the same time. The reason for this occurrence is not completely understood, but it most likely results because our ability to balance the heat flow in the retort is poor at very slow heating rates and too much heat was added.[12] A retort temperature profile at 95 hours is shown in Figure 7 that demonstrates the distortion of the thermal wave in the bottom 40% of the retort.

By comparing the concentrations of C_3H_8 produced at 60 and 78 hours and knowing that essentially all C_3H_8 comes from kerogen pyrolysis, the contributions of kerogen pyrolysis and associated reactions to the H_2 and H_2S concentrations have been determined by simple proportions and are noted by the double arrow in Figure 4. Again we see that about two-thirds of the H_2S generation occurs during kerogen pyrolysis. In contrast, most H_2 production comes from other sources, predominantly char gasification as discussed above.

Kerogen pyrolysis and C_3H_8 evolution is completed by 90 hours, but the H_2S production continues at a low level producing nearly constant concentration of 0.08%. Based on the steam-pyrite rate measurements reported earlier,[6] it is probable that the pyrite is mostly reacted by 95 hours, at least in the smaller particles. Given the essentially isothermal profile in the bottom 40% of the retort and the relatively slow gas velocities, it is also possible that the steam-pyrrhotite reaction is at equilibrium.

The first step in checking this premise is to determine the oxidation state of the iron so that the correct iron sulfide reaction can be chosen. The iron oxidation state can be determined from either the H_2O/H_2 or CO_2/CO ratio if the water-gas shift reaction is at equilibrium.[13] The steam concentration is calculated from the measured nitrogen concentration, the relation from the inlet composition that $N_2/H_2O = 0.78$, and the assumption that the water consumed by char gasification is approximately cancelled by the water produced by combustion of hydrogen in char and gases and from high-temperature dehydration of clays. After renormalization to 100%, the gas composition at 527°C near the end of the retort is given in Table 4. From these concentrations, it is easily shown that the water-gas shift reaction is within 25% of equilibrium.[14] This results in an oxygen partial pressure of 10^{-26} atm, which implies that iron sulfide is oxidized to Fe_2O_3.[13] The equilibrium expression for the reaction

$$FeS + \frac{3}{2} H_2O = \frac{1}{2} Fe_2O_3 + H_2S + \frac{1}{2} H_2 \qquad (1)$$

is given by[14]

$$K_1 = P_{H_2S}\, P_{H_2}^{0.5}\, P_{H_2O}^{1.5} = 1.7 \times 10^{-4} \text{ at } 527°\text{C} .$$

Substituting the concentrations into this expression and solving for P_{H_2S} results in $P_{H_2S} = 0.02\%$, which is reasonably close to the observed concentration of 0.05%. This result makes the pyrrhotite-steam equilibrium plausible. However, diffusion limitations for the steam-iron sulfide reactions in the larger particles complicate the analysis.

One of the more difficult results to understand is that of COS shown in Figure 5. Less is known about its mechanism of formation than other gas species discussed in this paper. Its highest concentration in the experiment occurred during ignition, probably due to the lack of steam during ignition. The next highest concentration occurred at 21 hours, the same time that other species show minor peaks in concentration. The reason for this peak is not known, but may be related to the steam front reaching the bottom of the retort shortly before. As for CO, the rate of COS production increased when the steam flow was interrupted. The increase in COS concentration between 60 and 77 hours is comparable to that of CO and H_2, whose major source of production is char gasification at temperatures substantially greater than kerogen pyrolysis. Like H_2S, and unlike CO and H_2, the COS concentration at 96 hours drops to a plateau substantially lower than its value at 60 hours. From these results alone, it is difficult to decide by what reactions and in what temperature range COS is formed.

In a laboratory experiment,[15] the rate of COS evolution was measured from a sample representative of the lean shale in L-4 (77 ℓ/Mg, Tract C-a, 560 ft.) as it was heated at a rate of 2°C/min. The COS generation rate peaked near 400°C, decreased gradually during oil generation, and remained low until 750°C when the experiment was terminated. Similar behavior has been observed previously for H_2S. This suggests that concentrations of COS in combustion retorts might be estimated from assay gas analysis. Subsequent re-examination of data from LLNL assays revealed that COS had been detected (detection limit of 100 ppm) only in high-sulfur samples from Tract C-a. Three of the samples were the same as materials used in LLNL retort runs L-3 and S-20. COS/C_3H_x values of 2.8×10^{-2} and 1.0×10^{-2} in the assay gas from the shale in the top and bottom, respectively, of retort run L-3 (steam-air) agree very well with the retort values of 2.9×10^{-2} and 1.1×10^{-2}. However, the assay COS/C_3H_x value of 7.2×10^{-2} for the 63 ℓ/Mg material used in S-20 is lower than the average value of 0.2 observed near the middle of retort run S-20 (air). Also, 100 ℓ/Mg material from Anvil Points gives COS/C_3H_x ratios less than 3×10^{-3} in the assay gas, but retort runs using similar material gave COS/C_3H_x ratios of 6.7×10^{-2} (L-1, air), 1.5×10^{-2} (L-2, Steam-air), and 5.3×10^{-2} (S-23, CO_2-O_2). The relationship between COS concentrations in assay gas and retort offgas is not completely understood.

One explanation which appears to fit most of the data is that COS is a secondary product from H_2S. Two possible reactions are

$$H_2S + CO_2 = COS + H_2O \tag{2}$$

and

$$H_2S + CO = COS + H_2 \quad . \tag{3}$$

Both of these reactions are similar to the water-gas shift reaction. If they are catalyzed by iron oxides or sulfides, they may proceed by analogous reaction intermediates. These reactions would explain why the peak COS evolution rate is at approximately the same temperature as for H_2S. They would also explain why the presence of steam appears to depress COS concentrations in the LLNL combustion retorts, because a 50% steam diluent increases both steam and hydrogen concentrations much more than H_2S concentrations.

As for the water-gas shift and steam-iron sulfide reaction, it is relatively easy to determine if reactions (2) and (3) are close to equilibrium near the end of retort run S-24. The equilibrium constants[14] of reactions (2) and (3) at 527°C are $K_2 = 30$ and $K_3 = 270$. Since the water-gas-shift reaction is close to equilibrium, both of these equations give the result that the COS/H_2S ratio is approximately 10% of its equilibrium value. Apparently the reaction rates of these reactions are slower than the water-gas-shift and steam-iron sulfide reactions, possibly because of the low COS concentrations.

The final reactions discussed deal with organic chemistry. Steam has been shown to favorably affect oil yields from small particles.[16,17] When the steam flow was interrupted in retort run S-24, the CH_4/C_3H_x ratio dropped by a factor of 1.2. This result is not understood at this time.

Another unexplained, but more important, effect of steam is to decrease the pour point of the oil. Most of the LLNL retorts used Anvil Points oil shale with a grade of about 100ℓ/Mg. For the eight non-steam runs that used this material (S-7, 9, 10, 11, 12, 17, 23 and L-1), the reported pour points ranged from 6 to 23°C, with an average of 15°C. For the eight retort runs with steam diluent of 50 to 75% (S-13, 14, 15, 16, 18, 19, 24, L-2), the reported pour points ranged from -10°C to -1°C, with an average of -5°C. The reason for this effect is unknown. An exception is the pour point of 24°C for run S-21, which had an inlet gas of 90% steam and 10% O_2. Perhaps the oil-water separation difficulties encountered for this case changed the nature of the oil. The effect is perhaps also present, but to a much smaller extent, in the shale oil from the settling-bed retort at LLNL, which used a very similar material. The pour points of the two experiments with inlet steam concentration near 60% are 20 and 25°C. For the two experiments with inlet steam concentration near 70%, the pour points are 13 and 8°C. The effect of steam on pour point is apparently much less pronounced at rapid heating rates typical of surface processes.

SUMMARY

Steam has several important effects on the composition of offgas from combustion retorts. The most pronounced effect is the 2.5- to 3-fold increase in hydrogen concentration. The results from the steam-interruption experiment reported in this paper are consistant with conclusions drawn previously from total generated gases.[1,2]

Steam can also have a pronounced effect in increasing the amount of carbonate decomposition, hence CO_2 concentration in the offgas, if the peak temperature in the retort is low enough that a significant fraction of the carbonates would not decompose in its absence and if the particles are small enough for the steam to diffuse into them. The peak temperature was 740°C during the time when the steam flow was interrupted in S-24. In this case, the drop in CO_2 concentration from 35 to 25% corresponds to a threefold reduction in the rate of carbonate decomposition. This effect is consistant with laboratory results reported earlier.[5]

The effect of steam on sulfur-containing gas species in significant. The quantity of H_2S production per unit shale processed increases by a factor of 1.4 for Anvil Points oil shale. This increase is caused by the steam-pyrite reaction. However, thermodynamic constraints severely limit the extent of the steam-pyrrhotite reaction. Both of these effects are consistent with previously reported laboratory studies.[6] They are also consistent with sulfur balance calculations from previous retorts. Steam also appears to cause a decrease in the concentration of COS in the retort offgas. This effect is attributed to reactions analogous to the water-gas-shift reaction.

Finally, it is observed that steam in the retort significantly lowers the pour point of oil produced. Most retort runs with Anvil Points oil shale that used a steam diluent had pour points less than the freezing point of water. The cause for this effect is unknown.

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TABLE 1

Gas inlet flow rates (ℓ/min.) during LLNL retort run S-24.

TIE, Hours	Air	Steam	N_2
3.4 to 4.2	18	0	0
4.2 to 4.8	4.1	0	0
4.8 to 50.9	4.1	4	0
50.9 to 51.9	4.1	0	0
51.9 to 103.4	4.1	4	0
103 to 150	0	0	6.3

TABLE 2.

Change in the rate of gas production between 51.0 and 52.1 hours into LLNL retort run S-24. The changes are due to the interruption of inlet steam flow while an air flow of the same rate remained constant.

Gas	Change	Factor
H_2	decrease	2.6
CO_2	decrease	1.7
H_2S	decrease	1.5
CH_4	decrease	1.4
C_3H_x	decrease	1.2
CO	increase	1.5
COS	increase	1.6
Total	decrease	1.3

TABLE 3

Comparison of sulfur distribution in products from combustion retort experiments with and without steam diluent.

Product	Non-Steam Runs S-10,11,12,17,20,23	Steam Runs S-13,14,15,16,18,19,21
Spent Shale	0.62	0.51
Oil	0.10	0.09
Gas (by difference)	0.28	0.40

TABLE 4

Gas composition near the end of the retort at 95 hours calculated from the dry-gas composition and an equimolar steam-air inlet

Gas	Vol. %	Gas	Vol. %
H_2O	34	N_2	27
H_2	4.6	H_2S	0.05
CO	1.2	COS	4.0 ppm
CO_2	30		

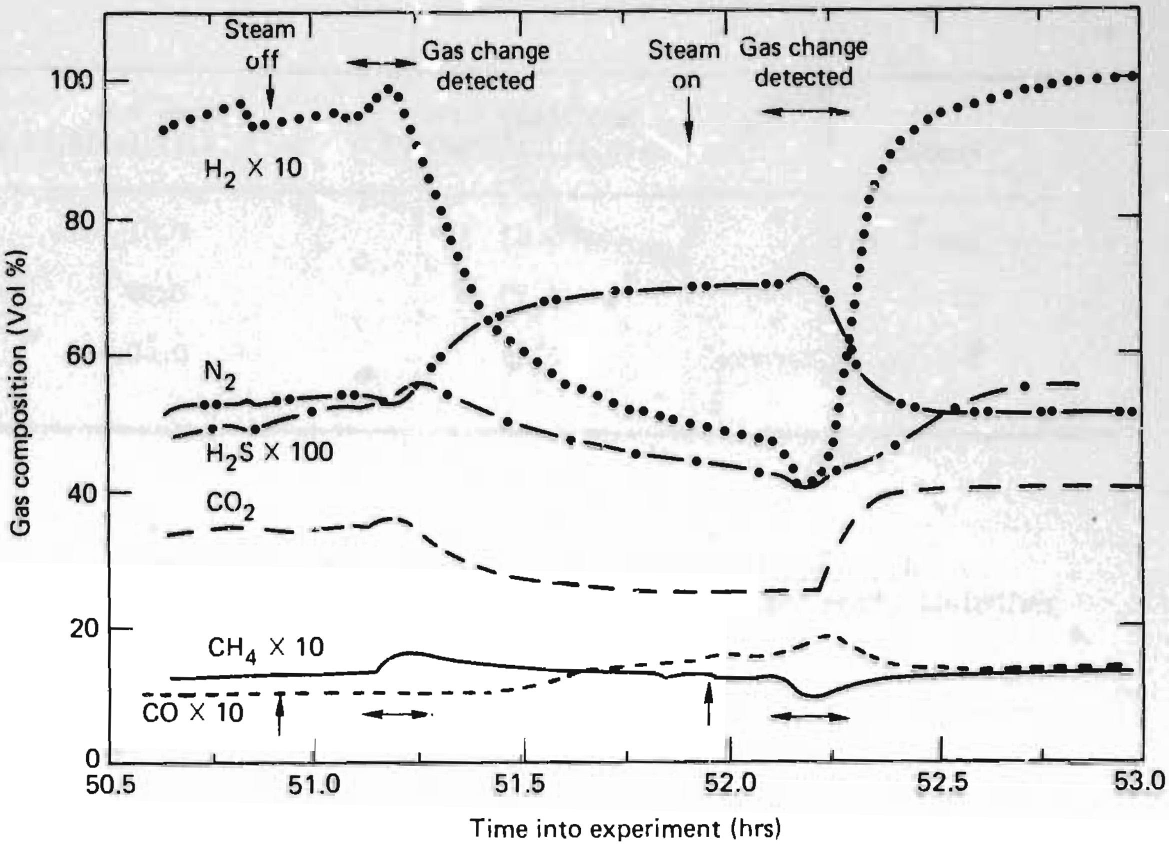

Figure 1. Change in gas composition during a one hour interruption of steam flow during LLNL retort run S-24. CO concentrations were determined by gas chromatrography. Other species were determined by mass spectroscopy.

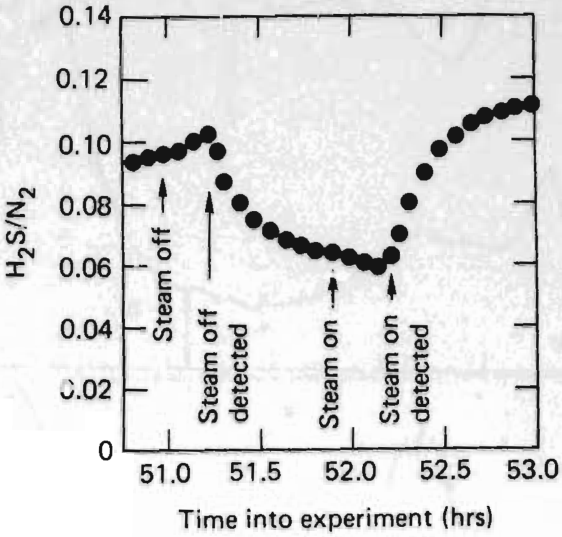

Figure 2. Decrease in the rate of H_2S production due to the interruption of steam flow into the retort. The air flow remained constant.

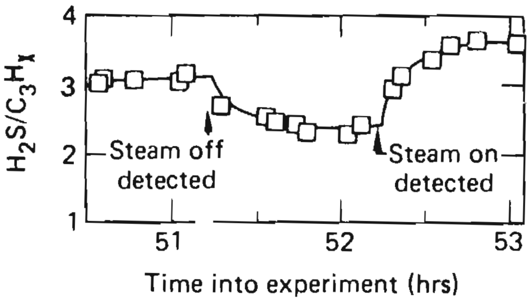

Figure 3. Change in the ratio of H_2S and oil generation rates as determined from the H_2S/C_3H_x hydrocarbon ratio. The line is merely a smooth curve drawn through the data points.

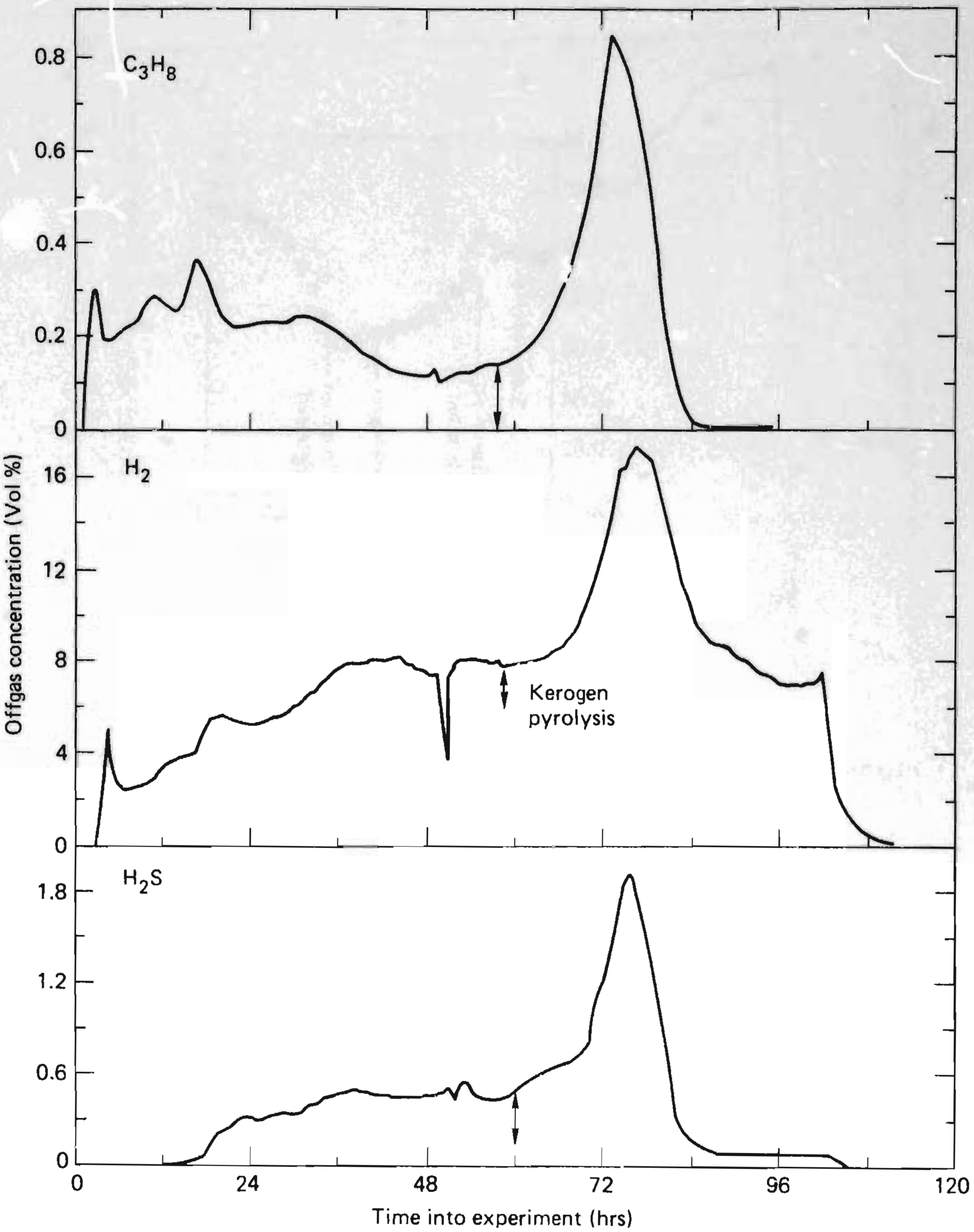

Figure 4. Concentrations of C_3H_8, H_2, and H_2S during retort run S-24. The C_3H_8 and H_2 concentrations were determined by gas chromatography. The H_2S concentrations were determined by mass spectroscopy.

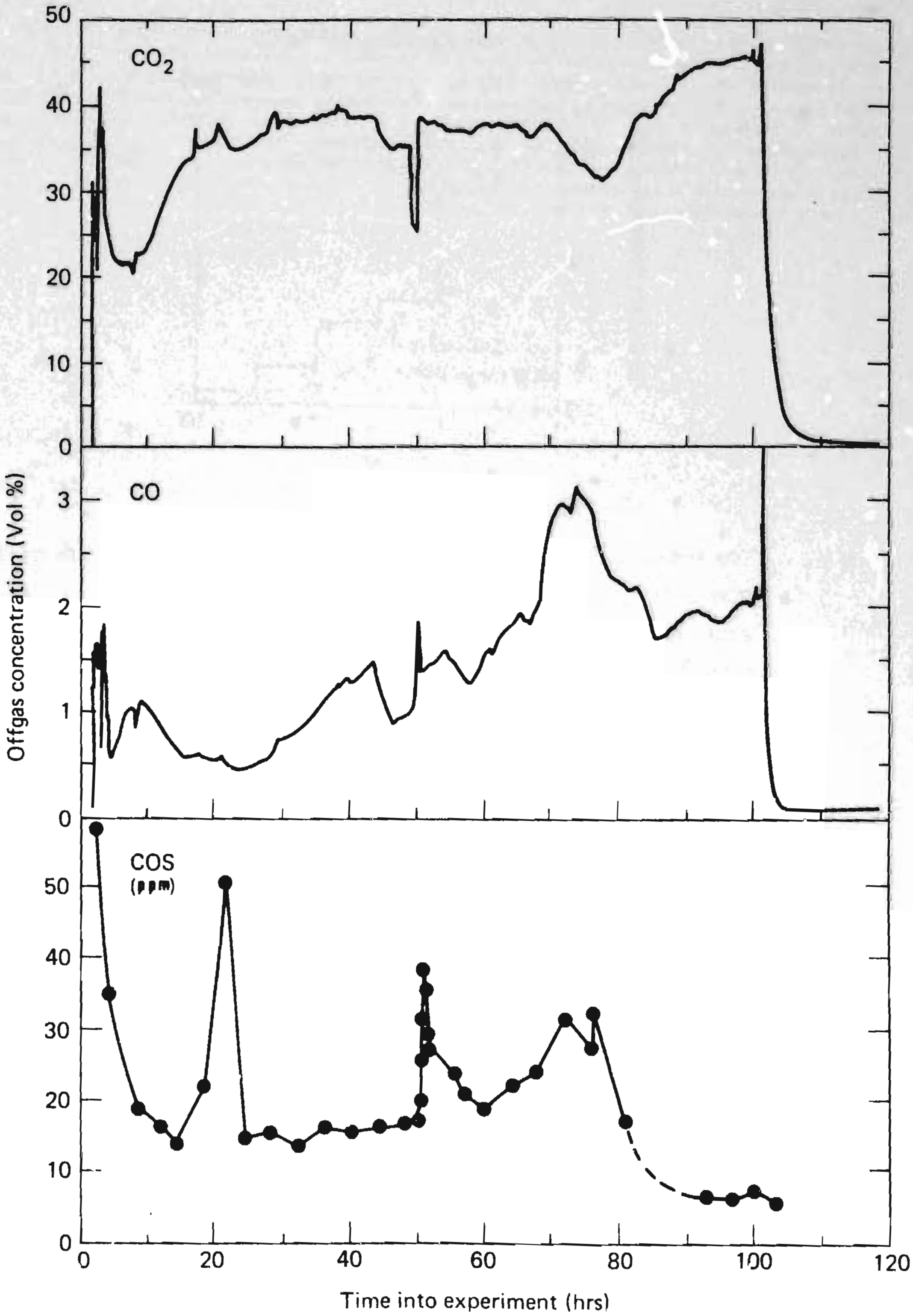

Figure 5. Concentrations of CO_2, CO, and COS during retort run S-24. The CO and CO_2 concentrations were determined by infrared meters. The COS results are from microwave spectroscopy.

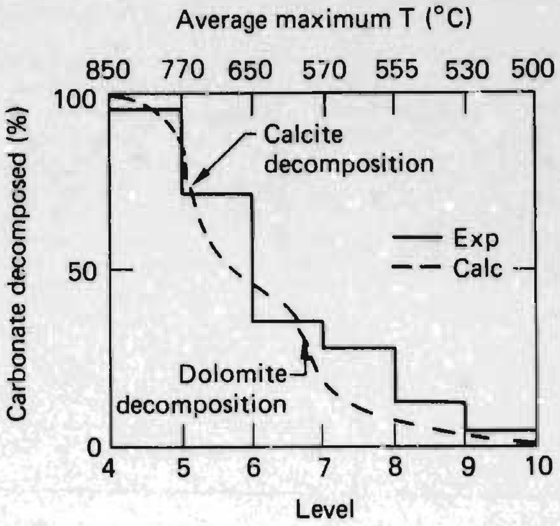

Figure 6. The extent of carbonate decomposition in the bottom 60% of retort run S-24. The extent of decomposition in the bottom three levels exceeds by a factor of 2.6 that calculated using Campbell's non-steam kinetics[8] and the experimental temperature history.

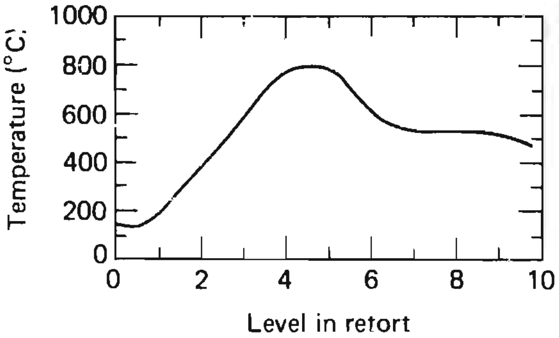

Figure 7. Centerline temperature profile of retort run S-24 at 95.3 hours as determined by a traveling thermocouple.

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