1 of 1

Adiabatic Calorimetry (RSST and VSP) Tests with Sodium Acetate

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DATE: August 17, 1993

TO: Dave Turner, WHC

FROM: Hans Fauske, FAI

SUBJECT: Adiabatic Calorimetry (RSST and VSP) Tests With Sodium Acetate

REFERENCE: "Energetics of Organic Compounds in Single-Shell Tank Waste",
Letter from R. J. Cash to H. K. Fauske dated May 5, 1993.

Summary

As requested in the subject reference, adiabatic calorimetry (RSST and VSP) tests have been performed with sodium acetate covering TOC concentrations from 3 to 7% with the following results:

- Exothermic activity noted around 200°C.
- Propagating reaction initiated at about 300°C. Required TOC concentration for propagation estimated at about 6 w% (dry mixture) or about 20 w% sodium acetate.
- Heat of reaction estimated to be 3.7 MJ per kg of sodium acetate (based on VSP test with 3 w% TOC and using a dry mixture specific heat of $1000 \text{ J kg}^{-1} \text{ K}^{-1}$).

Based upon the above results we estimate that a moisture content in excess of 14 w% would prevent a propagating reaction of a stoichiometric mixture of fuel and oxidizer (~ 38 w% sodium acetate and ~ 62 w% sodium nitrate). Assuming that the fuel can be treated as sodium acetate equivalent, and considering that the moisture content in the organic containing waste generally is believed to be in excess of 14 w%, it follows that the possibility of propagating reactions in the Hanford waste tanks can be ruled out.

RSST - 7 w% TOC (Recipe 3 in the Subject Reference)

A 9.75 gm 7 w% TOC sample (24 w% sodium acetate, 12 w% sodium hydroxide, 51.4 w% sodium nitrate and 12.6 w% sodium nitrite) was ground using a mortar and pistol and sieved to a 140 Mesh (105 micron) in a dry nitrogen filled glove box. Note that reagents were newly required and of purity levels required to satisfy those specified in the subject reference. Following loading of the sample in the RSST, it was subjected to an external heating rate of approximately 1°C/min.

The measured RSST data are presented in Figures 1 through 5. An Arrhenius type reaction is apparent at about 200°C but changes to a propagating reaction at about 300°C. The temperature jumps from 311°C to 363°C within one data point and then reaches a peak temperature of about 1067°C in the next point, 1.1 sec later. The corresponding pressure spike is about 160 psig. Cooldown pressure indicates a net increase of about 44 psi.

Considering the measured temperature rise of about 867°C and setting the specific heat equal to 1000 J kg⁻¹ K⁻¹, we calculate a heat of reaction of about 3.6 MJ per kg of sodium acetate.

Moles of gas produced can be estimated from the measured RSST containment pressure increase (following cooldown) by

$$\Delta n_{\text{moles}} = \frac{\Delta P V}{RT} \quad (1)$$

where ΔP (atm) = RSST containment pressure increase,
 V (l) = RSST containment volume (~ 0.35 l),
 R (l-atm/K-mole) = gas constant (0.08205), and
 T (K) = cooldown temperature (~ 295K),

and results in 0.044 moles of gas produced. This value is in good agreement with the calculated value (~ 0.043) based on the assumption that one mole of sodium acetate produces 1.5 moles of gas

FIGURE 1: SELF-HEAT RATE DATA FROM A034-18

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FIGURE 2: PRESSURE RISE RATE DATA FROM A034-18

FIGURE 3: TEMPERATURE DATA FROM A034-18

FIGURE 4: PRESSURE DATA FROM A034-18

FIGURE 5: PRESSURE/TEMPERATURE DATA FROM A034-18

Post test examination following cooldown indicates a reasonable violent reaction. The majority of the material in the test cell has been ejected from the cell. The containment walls are covered with a moist blackish film. Small hardened "pools" of a slightly brownish white solid are found on the vessel lid, floor, and on the insulation holder. In contrast to previous observations with propagating ferrocyanide reactions, the test cell is not broken. It contains only a small hardened pool of the brownish white solid at the bottom. The material has a lot of void space in it, suggesting that gas was being produced when it solidified. Overall good reproducibility of the above findings have been demonstrated by performing duplicate tests. The measured cooldown pressures ranged from 40 to 45 psi.

RSST - 5 w% TOC (Recipe 2 in the Subject Reference)

A 9.97 gm 5 w% TOC sample (17.2 w% sodium acetate, 8.5 w% sodium hydroxide, 59.7 w% sodium nitrate, 14.6 w% sodium nitrite) was prepared and loaded in the RSST, using procedures similar to the RSST test - 7 w% TOC.

The measured RSST data are presented in Figures 6 through 10. Again, significant exothermic activity is noted close to 200°C, but in contrast to the 7 w% TOC test, no apparent transition to a propagating reaction is observed, despite reaching a peak temperature of about 670°C.

The above observation is consistent with the relatively lower measured cooldown pressure increase of about 8 psi, which is equivalent to about 0.008 moles of gas produced, as compared to a theoretical value of about 0.03 moles. Also consistent with these observations is the RSST measured temperature increase following exothermic activity of about 470°C which results in an equivalent heat of reaction of about 2.8 MJ per kg of sodium acetate.

Post-test examination following cooldown again indicate that a significant fraction of the test cell contents were ejected. The vessel

FIGURE 6: SELF-HEAT RATE DATA FROM A034-16

FIGURE 7: PRESSURE RISE RATE DATA FROM A034-16

FIGURE 8: TEMPERATURE DATA FROM A034-16

FIGURE 9: PRESSURE DATA FROM A034-16

FIGURE 10: PRESSURE/TEMPERATURE DATA FROM A034-16

walls and lid, however, were not covered with the moist black film that was noticed in previous 7 w% TOC tests.

RSST - 3.5 w% TOC

A 9.85 gm 3.5 w% TOC sample (11.8 w% sodium acetate, 8.5 w% sodium hydroxide, 62.9 w% sodium nitrate and 16.8 w% NaNO_2) was prepared and loaded in the RSST, using the same procedures as used for RSST test - 7 w% TOC.

The measured RSST data are presented in Figures 11 through 14. Exothermic activity is indicated around a temperature of about 180°C, although this indication may be due to the RSST overcompensating for an endotherm at the same temperature. Again, no apparent transition to a propagating reaction is observed. The net pressure gain following cooldown is about 5 psi which corresponds to about 0.005 moles of gas. This compares to the theoretical value of about 0.021 moles.

Post-test examination following cooldown showed similar behavior to that observed for RSST test - 5 w% TOC, i.e., the absence of the moist black film that was noticed with 7 w% TOC tests.

RSST - 3 w% TOC (Recipe 1 in the Subject Reference)

A 9.90 gm 3 w% TOC sample (10.4 w% sodium acetate, 7.2 w% sodium hydroxide, 67.8 w% sodium nitrate and 16.8 w% sodium nitrite) was prepared and loaded in the RSST, using the same procedures as described for the RSST test - 7 w% TOC.

The measured RSST data are presented in Figures 15 through 19. Exothermic activity is again indicated around 180°C, although it is noted that this indication may be accelerated due to the RSST overcorrecting for a possible endotherm in the same temperature region. Again, no apparent transition to a propagating reaction is observed. The net pressure gain following cooldown is about 3 psi which corresponds to about 0.003 moles of gas produced. This compares to the theoretical value of about 0.019 moles.

FIGURE 11: SELF-HEAT RATE DATA FROM A034-I3

FIGURE 12: PRESSURE RISE RATE DATA FROM A034-13

FIGURE 13: TEMPERATURE DATA FROM A034-13

FIGURE 14: PRESSURE DATA FROM A034-13

FIGURE 15: SELF-HEAT RATE DATA FROM A034-17

FIGURE 16: PRESSURE RISE RATE DATA FROM A034-17

FIGURE 17: TEMPERATURE DATA FROM A034-17

FIGURE 18: PRESSURE DATA FROM A034-17

FIGURE 19: PRESSURE/TEMPERATURE DATA FROM A034-17

Assuming onset of exothermic activity at about 180°C, results in a measured temperature rise of about 305°C and a heat of reaction value of about 2.9 MJ per kg of sodium acetate.

Post-test examination following cooldown indicated similar behavior to that noted for RSST tests with 3.5 and 5 w% TOC.

VSP - 3 w% TOC (Recipe 1 in the Subject Reference)

A 60.29 gm 3 w% TOC sample (10.4 w% sodium acetate, 5.4 w% sodium hydroxide, 67.5 w% sodium nitrate and 16.7 w% sodium nitrite) was prepared and loaded in the VSP test cell, using the same procedures as noted for RSST test - 7 w% TOC. The subject test was carried out with the objective of measuring the adiabatic temperature rise to more accurately determine the heat of reaction associated with the exothermic activity.

The measured VSP data are presented in Figures 20 through 23. The general trends of the data are consistent with the corresponding RSST tests. Due to the VSP capability of accommodating endothermic behavior, noticeable exothermic activity is not suggested before about 200°C. Using this as the reference temperature, an adiabatic temperature rise of about 370°C is indicated with a peak temperature of 570°C. Both the RSST and the VSP tests indicate peak rates of about 200°C/min, but the peak temperature measured with the RSST test is about 475°C as compared to 570°C with the VSP test. This difference can be related to the much larger time constant for the VSP sample, allowing the larger sample to more closely approach adiabatic heatup conditions (i.e., the time constant is large compared with the time associated with the noted temperature rise). On this basis we estimate a heat reaction of about 3.7 MJ per kg of sodium acetate using a heat capacity value of $1000 \text{ J kg}^{-1} \text{ K}^{-1}$.

The net pressure gain following cooldown in the VSP containment vessel (3.75 l) was 10 psi which corresponds to a gas production of 0.11 moles. This compares to the theoretical value of about 0.12 moles. Post-test examination of the VSP containment vessel indicated similar behavior to that observed with RSST tests 3, 3.5 and 5 w% TOC.

FIGURE 20: SELF-HEAT RATE DATA FROM A034-19

FIGURE 21: PRESSURE RISE RATE DATA FROM A034-19

FIGURE 22: TEMPERATURE DATA FROM A034-19

FIGURE 23: PRESSURE DATA FROM A034-19

Discussion

Based upon the above observations, it is of interest to estimate the necessary weight fraction of water that would prevent a propagating reaction with a specified acetate-nitrate mixture given the presence of an ignition source. Accounting for sensible as well as latent heat of vaporization due to the presence of water, we can estimate the weight fraction water that would prevent propagation from

$$x_{\text{H}_2\text{O}} > \frac{N}{1 + N} \quad (2)$$

$$N = \frac{(x - x_n) \Delta H_R - C_M(T_o - T_i)}{\lambda + C_{\text{H}_2\text{O}}(T_B - T_i)}$$

- where x - weight fraction of fuel (sodium acetate) in a dry mixture,
- x_n - estimated weight fraction of fuel (sodium acetate) in a dry sample to produce a propagating reaction ($x_n = 0.20$),
- ΔH_R (J/kg) - estimated heat of reaction per kg of sodium acetate (~ 3.7 MJ),
- C_M (J kg⁻¹ K⁻¹) - specific heat of dry sample (~ 1000 J kg⁻¹ K⁻¹),
- T_o (K) - onset temperature for propagating reaction (~ 573 K),
- T_i (K) - waste tank operating temperature (~ 323 K),
- λ (J kg⁻¹) - latent heat of vaporization ($\sim 2.25 \cdot 10^6$ J kg⁻¹),
- $C_{\text{H}_2\text{O}}$ (J kg⁻¹ K⁻¹) - specific heat of water (~ 4300 J kg⁻¹ K⁻¹), and

*The 0.2 value simply represents the average between 5 w% TOC and 7 w% TOC. Recall that the 5 w% TOC test did not exhibit a propagating reaction while 7 w% TOC test did.

T_B (K) - boiling temperature of waste (~ 403K).

Based upon the above parameters, we calculate the necessary weight fraction of water or moisture to prevent a stoichiometric mixture (~ 38 wt sodium acetate or 11 wt TOC, and 62 wt sodium nitrate) from propagating given an ignition source to be only about 0.14 (14 wt), suggesting that propagating reactions in the Hanford tank environment can be ruled out. Additional adiabatic calorimetry tests using sodium oxalate and sodium stearate representing the organic fuel are being planned to further confirm the above observation.

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Attachments

cc: R. J. Cash, WHC
D. W. Jeppson, WHC

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