Thermal and Spectroscopic Analyses of Caustic Side Solvent Extraction Solvent Contacted with 16 Molar and 8 Molar Nitric Acid

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Abstract: Thermal and spectroscopic analyses were performed on multiple layers formed when Caustic Side Solvent Extraction (CSSX) solvent was contacted with 16 M or 8 M nitric acid. A rapid (i.e., minutes to hours) chemical reaction occurs between the solvent and 16 M or 8 M nitric acid as evidenced by color changes and the detection of nitro groups in the infrared spectrum of the aged samples. Thermal analysis revealed that decomposition of the resulting mixture does not meet the definition of explosive or deflagrating material.

Keywords: ARC; Energetic, Infrared; Nitration

INTRODUCTION

After chemical analysis, Analytical Laboratories (analytical labs set up to support solvent extraction operations at Savannah River Laboratories) plan to discard aqueous residues from Modular CSSX Unit (MCU) sample analysis through the existing drain system. While the typical aqueous residue will contain only entrained CSSX solvent, Analytical Laboratories must also plan for the possibility of inadvertent discharge of pure solvent to the drains (the components and their concentrations are shown in Table 1 for CSSX solvent). Other discards to the drain system may include 8 to 16 M nitric acid, especially during evolutions to flush the lines and tanks. Hence, there is a possibility that CSSX solvent (whether entrained or pure) may contact concentrated

Table 1. Component concentration of CSSX solvent

Component	Concentration
BobCalix extractant	0.007 M (~1 wt %)
Cs-7SB modifier	0.75 M (~29.7 wt %)
Tri-Octylamine	0.001 M
Isopar®L	(69.1 wt %)

nitric acid solution and yield energetic compounds and produce gases from the resulting reaction.

Oxidation and nitration reactions between aromatic compounds and concentrated nitric acid have long been investigated (1–8). An examination of the molecular structure for the CSSX solvent components in Table 1 clearly show both the modifier and the extractant contain benzene rings susceptible to nitration. One previous study showed a possible reaction between 3 M nitric acid and the CSSX components (8) but higher nitric acid molarity was not evaluated. To this end, SRNL conducted contact tests of 16 M and 8 M nitric acid with CSSX solvent and monitored the system for reactions and formation of energetic materials. Additional work in progress examines the interaction of the solvent with 1 M and 3 M nitric acid.

EXPERIMENTAL TESTING DESCRIPTION

CSSX solvent was contacted with either 16 M or 8 M nitric acid at a ratio of one to three (organic to aqueous), by volume, in square bottles. With this ratio, the reaction is not reactant limited and sufficient quantities of degradation products are available for the different analytical tests. Also, contact without mixing guarantees the highest spatial concentration of nitrated material. Mixing increases the rate of formation but does not increase the degree of nitration. Moreover, the nitrated material is dispersed over a larger volume of aqueous solution with agitation which would decrease the likelihood of self-initiating reactions.

The bottles were monitored by visual observations (photographs) and measured the solution color by UV-vis (ultraviolet-visible) spectroscopy. In addition, they measured various fractions from the reaction bottles using Fourier transform infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) spectroscopy. These two techniques provide insight into the molecular structure of the organic molecules present in the respective layers. A Nexus® 760 and Bruker® 300 MHZ Magnet

was used to characterized the samples. For the FTIR work about 200 scans were collected at resolution of $4\,cm^{-1}$ and a triangular apodization was applied before Fourier transforming the interferogram. For the magnetic resonance work, about 65536 scans were collected running a ZG-30 (zero go at $30°$ magnetization pulse) hydrogen decoupled carbon NMR program.

For thermal characterization, the United Nations (UN) recommends that at least three explosion tests are conducted to determine the explosion hazard of substances (9). These tests were designed for the safe transportation of substances. The three tests recommended include the GAP test (for testing the propagation of explosion), Koenen test (for testing thermal sensitivity in enclosures), and the Time/Pressure test (for testing deflagration behavior in a closed enclosure). Both the Koenen and Time/Pressure tests are applicable to determining the thermal sensitivity and consequence of decomposition of energetic materials resting in a drainage piping system.

The lab has a Differential Scanning Calorimeter (DSC) that is more sensitive in detecting heat and heat rate than the instruments used in the UN recommended tests. Fortunately, correlations have been established between the results from the UN tests and DSC results with known explosives that can be used to evaluate the thermal hazard of unknown materials (10). To determine the thermal behavior of the samples, personnel removed portions from the organic, interface, and aqueous layers from the bottle and analyzed them by Differential Scanning Calorimetry (DSC) to detect the formation of energetic compounds (indicated by presence of exothermal events in the scanning). Samples were heated at $20°C/min$ in Perkin Elmer DSC 7. Cooling curves only revealed a baseline response from the decomposed material and it did not relate to the initial baseline during heating.

To examine the rate of gas generation from the decomposition reaction, personnel added 1 wt % acid-contacted, or "aged," organic from the interface layer to organic-contacted, or "aged," nitric acid (i.e., 16 or 8 M nitric) and adiabatically heated the mixture in an Accelerated Rate Calorimeter (ARC). This ratio of "aged" organic to "aged" nitric acid is well above the ratio expected for the organic in the Analytical Laboratories drain system. The ARC provides data on the highest pressure and temperature reached as well as the rate of pressurization and heating from any self-heating reactions. Both thermal analysis methods are typically used to determine the thermal hazards of materials. A TIAX(r)2000 from TIAX, INC. was used to run adiabatic heating programs that included heating the samples $5°C$, then wait for 20 minutes looking for self-heating above $0.2°C/min$, and if not reaction occurred, then the sample was heated another $5°C$.

RESULTS AND DISCUSSION

Figure 1 shows chronometric progression of the dark color change observed when the solvent is in contact with 16 M or 8 M nitric acid. Figure 1 clearly shows the reaction occurred much faster in the 16 molar nitric acid contact test leading to formation of visible NO_x gases (after 24 hours). The effect of lower nitric acid molarity (such as 8 M) is slower kinetics but we suspect that the final products and reactivity will be similar for the 8 M as in the 16 M nitric acid.

An infrared spectrum of the visible red-orange layer in the interface of CSSX solvent with 16 M nitric acid revealed the presence of the NO_2 molecular group as shown in Fig. 2. Inspection of Fig. 2 reveals the selective nitration of the modifier (Cs-7SB); the BobCalix extractant is not believed to contribute nitrated degradation products due to its unfavorable carbon-hydrogen-oxygen ratios and low concentration in CSSX solvent. The NO_2 peak at $1533\,cm^{-1}$ indicates an aromatic ring nitration and not an aliphatic nitration on the modifier (absorption expected between 1601 and $1534\,cm^{-1}$ for aliphatic nitro groups) (11). The spectra also show the CSSX layer from the test bottle is depleted in modifier (top spectrum in Fig. 2). This indicates selective nitration/oxidation of the modifier. No low molecular weight molecules such as tri-nitrotoluene (TNT) were observed in Fig. 2. The infrared absorption peak positions for molecules such as TNT are shown in Table 2, and none of these absorptions match the $1533\,cm^{-1}$ band observed for the interfacial compounds.

To shed more light on the infrared data, personnel conducted ^{13}C NMR of the aqueous layer removed after two months from the 16 M test. By this time, the organic compound produced in the interfacial layer was
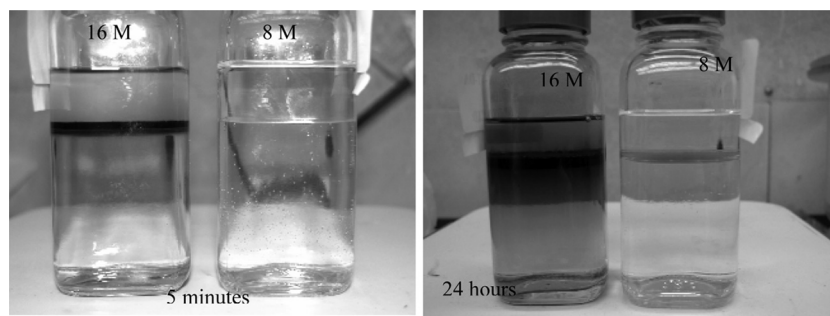
Figure 1. An optical picture of MCU (Modular Caustic Side Solvent Extraction Units) in 16 M nitric acid (left bottle) and 8 M nitric acid (right bottle).
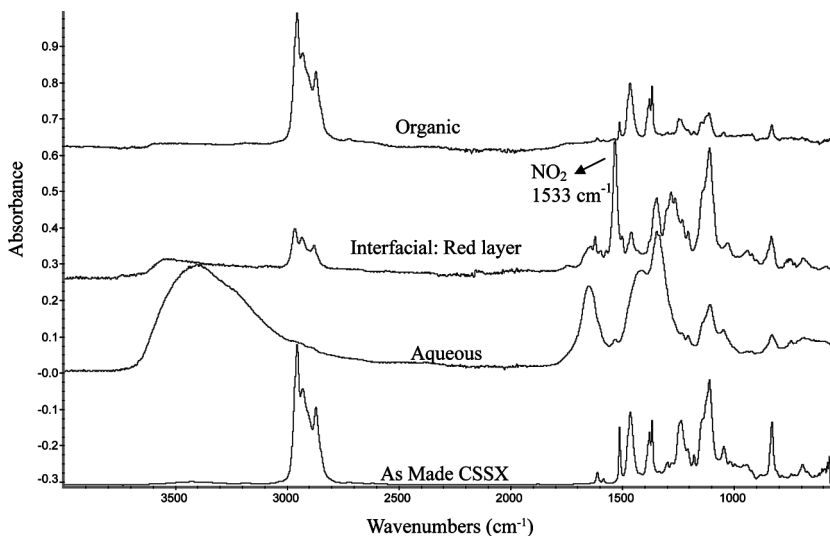
Figure 2. An FT-IR of the layers seen in Fig. 2.

well dispersed in the aqueous layer. This data is shown in Fig. 3. Also shown in Fig. 3 is the spectrum of "As Received" modifier (Cs-7SB) for comparison. An inspection of the spectra shown in Fig. 3 clearly shows that the organic residue found in the aqueous portion of the test (after 2 months) does not have any aliphatic structure. The NMR spectrum indicates a substituted aromatic molecule that includes a nitro group.

To determine the energetic of the nitrated organic, we performed thermal analysis to determine energies of the decomposition reaction. Researchers removed portions of the organic, interface, and aqueous layers from the solvent/16 M nitric acid solution and conducted DSC scans for each portion. Figure 4 shows the DSC thermogram from each portion of the solution. Inspection of Fig. 4 shows the presence of broad exotherms in the scan of the interface layer as well as the scan for the aqueous layer. The exotherm peaks below 200°C were not sufficient to raise the temperature enough to set off the exotherm peak since above 200°C. The specific thermal degradation reaction occurring below 200°C was not possible to identify. A much sharper exotherm is seen in the scanning of the organic layer (CSSX solvent). The amount of heat generated during decomposition of the samples as well as the onset temperature is listed in Table 3. Inspection of Table 3 shows the decomposition energy density ΔH, the onset temperature T_o, and algebraic manipulations of the two quantities that have been correlated to

Table 2. Infrared adsorption bands for TNT, ortho-MNT, para-MNT, RDX and PETN

Sample	Band (cm^{-1})	Integrated Absorption (cm^2/mol^{-1})
TNT	1080	383
	1349	1.05 E4
	1402	648
	1559	1.56 E4
	1606	1.02 E3
	2898	359
	3107	642
Ortho-MNT	1216	3.73 E3
	1366	4.05 E3
	1736	8.15 E3
Para-MNT	1216	706
	1356	5.94 E3
	1547	5.76 E3
	1608	1.38 E3
	1737	1.56 E3
RDX	1272	4.17 E4
	1602	2.16 E4
PETN	1279	4.13 E3
	1626	2.34 E4

From J. Janni, B. D. Gilbert, R. W. Field, and J. I. Steinfeld, "Infrared Absorption of Explosive Molecule Vapors," Spectrochimica Acta Part A, 53 (1997) pp 1375–1381.

TNT = Tri-NitroToluene.
MNT = MonoNitroToluene.
RDX = Penclotrimethylene trinitramine.
PETN = Pentaerythritol tetranitrate.

explosive detection testing from the literature (10). Also shown in Table 3 is the target value (criteria) for the energetic to be classified as explosive. As shown in Table 3, after aging for 24 hours, none of the layers from the 16 M nitric acid solution decomposed to form compounds displaying characteristics associated with explosives.

Discussion of ARC Analyses

The DSC does not measure pressure released during decomposition; the ARC measures scale-up effects for pressurization and heating. A literature search identified a correlation exists between ARC results and the thermal decomposition of known explosives (12). Table 4 shows the
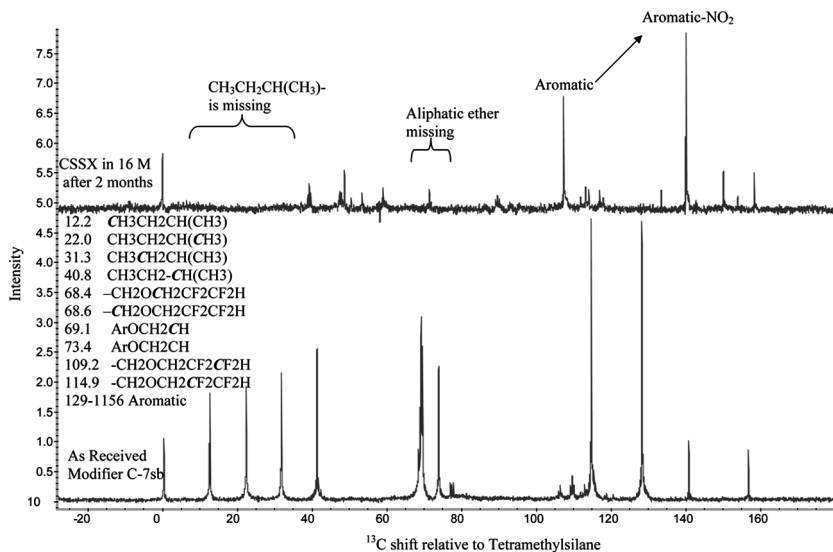
Figure 3. The ^{13}C-NMR spectrum of CSSX exposure to 16 M nitric acid for 2 months is shown in the upper trace. The lower trace shows the ^{13}C-NMR spectrum of "As Received" Modifier C-7sb.
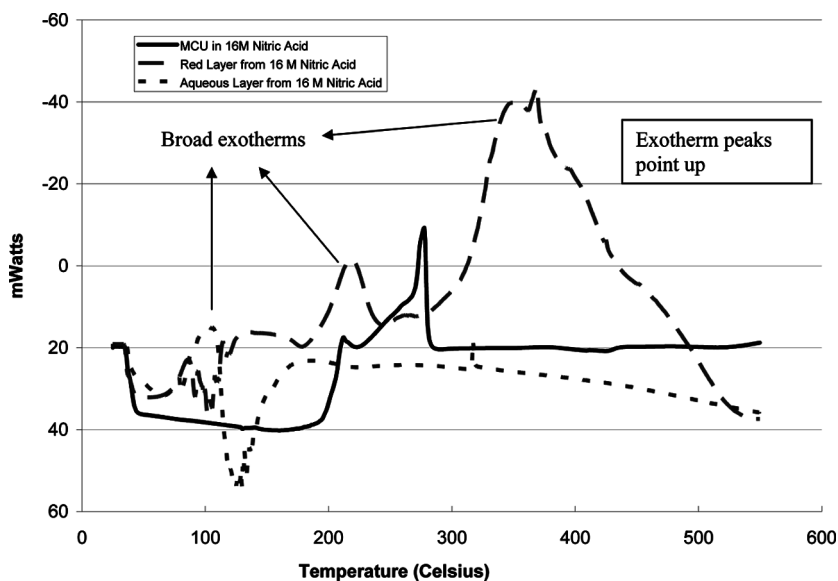
Figure 4. The DSC scanning of the three different layers created after 24 hours of contact between CSSX solvent and 16 M Nitric acid.

Table 3. Calorimetry parameters from the DSC Analysis of CSSX solvent in 16 and 8 M Nitric Acid

Sample identification	DH (J/g)	T_o (Celsius)	$DH/T_o^{0.5}$ [#] (correlates with GAP test)	DH/T_o [#] (correlates with Time/ Pressure test)	KP*[#] (correlates with Koenen test)
Solvent in 16 M Nitric Acid	139	196	10	0.7	−1495
Aqueous Layer from 16 M Nitric Acid	101	73	12	1.4	−8.2
Red Layer from 16 M Nitric Acid	475	275	29	1.7	−2138
Solvent in 8 M Nitric Acid	1.5	92	0.2	0.02	−343
Target value for Explosive[#]	>3000	<200	$>88\,J/g\,^{\circ}C^{0.5}$	>8.0	>0

KP = DH−(12.4 T_o −796).
[#]From Sanjeev R. Saraf, "Molecular Characterization of Energetic Materials," Ph.D. Thesis Texas A&M University, December 2003.

Table 4. Criteria for determining an explosive from an ARC result

Explosivity rank	Severest Class 1 property	Correspondence to UN classification	Preliminary breakpoints based on ARC dP/dt_{max} (Mpsi/min), T_{peak}(°C)
A	Detonates (positive result in UN Gap, or BAM 50/60 or TNO 50/70 if UN Gap unavailable).	Potentially Class 1	$dP/dt_{max} = 2.25$
B	Heating under confinement: violent (Koenen limiting diameter $\geq$ 2 mm), and/or Deflagration: Rapidly (pressure in Time/Pressure $\geq$ 2070 kPa in $<$ 30 ms)	Potentially Class 1 but not detonable	$0.25 = dP/dt_{max} < 2.25$ and $dP/dt_{max} = 0.04*T_{peak}$-5
C	Heating under confinement: medium or low (Koenen limiting diameter $\leq$ 1.5 mm), and /or Deflagration: slowly (pressure in Time/Pressure $\geq$ 2070 kPa in $\geq$ 30 ms)	Not Class 1	$0.25 = dP/dt_{max} < 2.25$ and $dP/dt_{max} < 0.04*T_{peak}$-5
D	No effect of heating under confinement, and does not deflagrate (pressure rise in Time/Pressure $<$ 2070 kPa)	No explosive properties with respect to transport classification	$dP/dt_{max} < 0.25$

From G. T. Bodman and S. Chervin, "Use of ARC in Screening for Explosive Properties," Journal of Hazardous Materials, Vol. 115, 2004, pp. 101–105.
UN = United Nations
UN GAP, UN BAM, and UN TNO are tests for explosive propagation, impact and thermal sensitivity of substances.

criteria that must be met by the decomposition of a material in the ARC to categorize the compound as explosive. In particular, emphasis is placed on the pressurization rate as a determining factor for detecting explosive behavior. The pressure rate data (along with the temperature rate data) is used to determine venting requirements.

About 1 wt % of aged solvent (from the interface) in aged 16 M and 8 M nitric acid solutions. The ratio of organic-to-aqueous was chosen to match the most probable conditions that would be present in the Analytical Laboratories drains if CSSX solvent were inadvertently disposed. The results from those tests are shown in Fig. 5 (16 M nitric acid) and Fig. 6 (8 M nitric acid). Inspection of both figures clearly shows self-heating behavior that leads to temperature rises beyond 100°C and pressures rises of several atmospheres. A summary of the physical parameters from the ARC tests is shown in Table 5.

For comparison with the criteria in Table 4, the derivative (dP/dt) was calculated for the data shown in Figs. 5 and 6. As shown in Fig. 7, the maximum pressure rate of 700 kPa/min (or 1.13 E-4 Mpsi/min) was observed for the 8 M nitric acid system. This pressure rate is (19.5 E3 times) less than 2.2 Mpsi/min, which is the threshold indicated in Table 4 for a reaction to be explosive. Also, the maximum pressure rate is low enough that the decomposition reactions observed here do not meet the threshold for a deflagration. The maximum pressure rate observed in the 8 M nitric acid test was 2.2 E3 times less than the
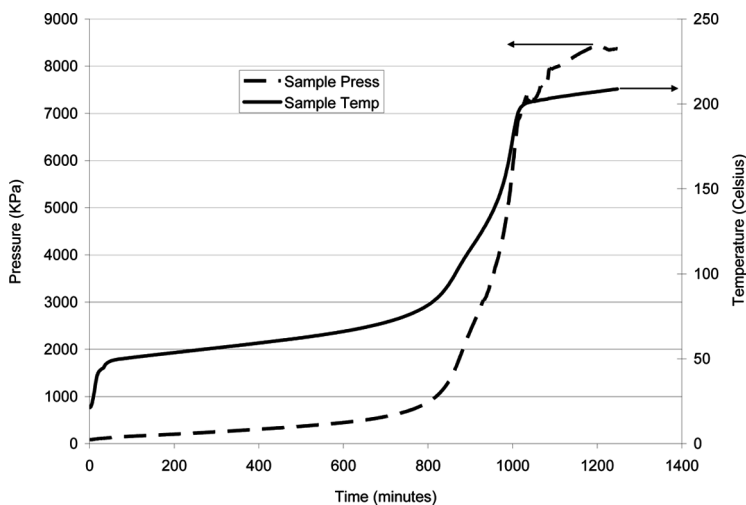
Figure 5. The temperature and pressure rise from the decomposition of 1 wt % aged CSSX solvent (24 hours) in aged 16 M nitric acid. (1 kPa = 1.45 E-7 Mpsi).
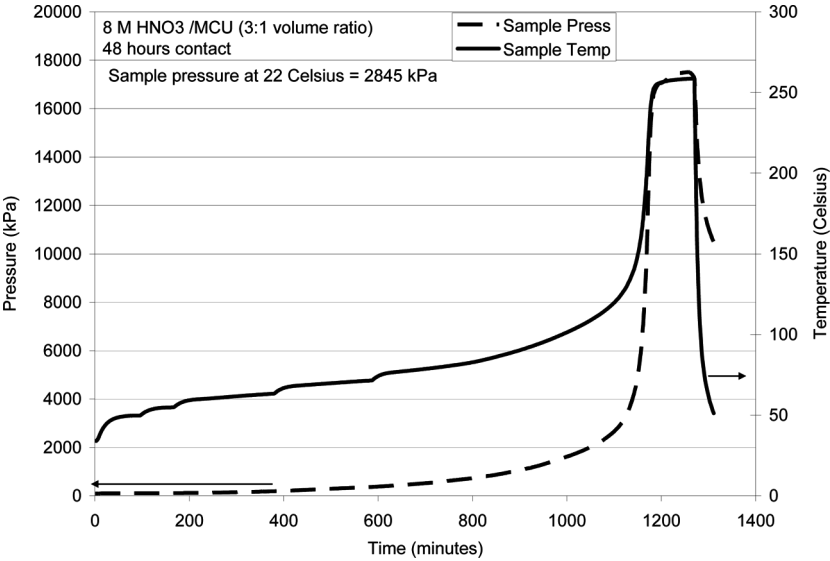
Figure 6. The temperature and pressure rise resulting from a decomposition of 1 wt % aged CSSX solvent (48 hours) in aged 8 M nitric acid.

0.25 Mpsi/min listed in Table 4. Interestingly, the pressure rate was higher from the decomposition of the 8 M nitric acid solution than from the 16 M nitric acid solution suggesting that, at higher nitric acid molarity (16 M), oxidation reactions dominate nitration reactions (by destroying nitrating species) in the degradation of organic material at room temperature. Dominant oxidative reactions have been seen in other nitric acid/re-resin reactions (13,14). The increased pressure rate in the 8 M nitric acid test is not due to an increase in yield for the reactive intermediate but it is due to the oxidation of the CSSX solvent by the 8 M nitric acid. Testing at 3 M and 1 M nitric acid showed a much smaller pressure and temperature rise. Therefore, the reaction of MCU organics with 8 M nitric acid

Table 5. A summary of the parameters obtained from the ARC tests

Sample	Pmax (Mpsi)	Tmax (Celsius)	dP/dt (Mpsi/min)	dT/dt (Celsius/min)
CSSX in 8 M Nitric Acid	2.54 E-3 17,517 (kPa)	266	1.13 E-4 777 (kPa/min)	6.0
CSSX in 16 M Nitric Acid	1.23 E-3 8,483 (kPa)	210	1.3 E-5 90 (kPa/min)	1.4
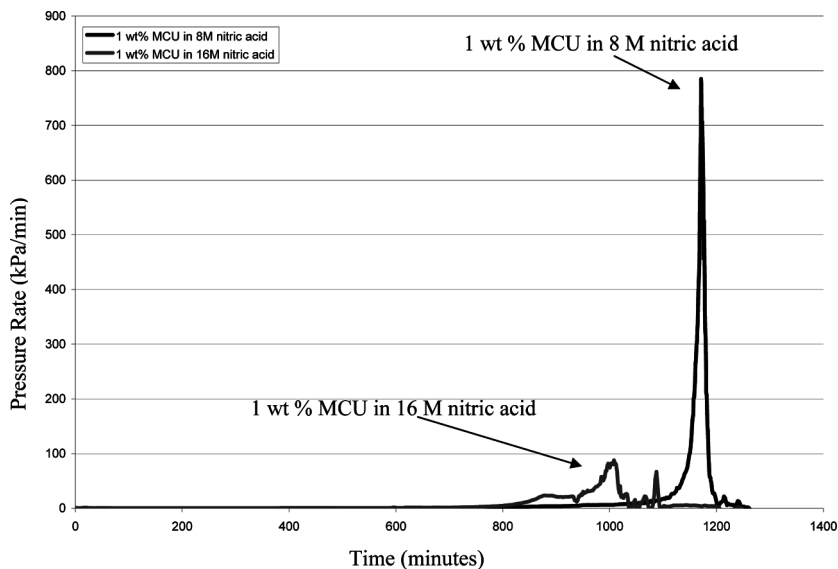
Figure 7. The pressure rate (kPa/min) obtained from the decomposition of CSSX solvent in 16 and 8 M nitric acid.

(and probably 5 M nitric acid) appears to be optimized the generation of energetic materials as well as the gas generation from the oxidation reaction. It is well known that at high nitric acid concentrations, the degree of nitric acid dissociation is small and nitric acid instead will form hydrates (mono and tri hydrates) (15). Therefore, a lower concentration of HNO_2 and NO_2^- species will be available for oxidation and/or nitration. At low nitric acid molarity (3 M or less), there are not any sufficient reactants such that reactions are aqueous transport limited. Therefore, optimal oxidation and/or nitration is expected somewhere in the 5 to 8 M nitric acid range.

Also note that agitating the sample (versus the bilayer configuration tested here) will increase the rate of nitration but not the extent of nitration since the latter is determined uniquely by the chemistry between nitric acid and the CSSX components. Agitation will also disperse the nitrated material faster into the aqueous solution (since the nitration makes the molecules more polar and therefore more soluble in water) and this dispersion will reduce the pressure and heat rate of the system. The presence of water intimately mixed with the nitrated material will attenuate the heat and gas given off by the thermal decomposition of the substance. Therefore, a more hazardous condition is created where all the nitrated material accumulates in a small spatial volume

(a concentrating mechanism) as was obtained in this test at the interfacial layer between CSSX and 16 M nitric acid.

Also, the extent of nitration (per organic molecule) obtained in this test is the highest that can be obtained since nitration is a chemical reaction dictated by molecular structure and chemical activity of substituents under the conditions tested. This test mixed two incompatible substances under conditions of temperature and pressure similar to conditions in the field (no external heating or pressurization). To increase the degree of nitration per molecule (and thus the energetics of the degradation products formed), much harsher conditions must be present than those associated with these tests or with the field conditions in the drain system. As shown by the collective data, the energy and gas generation rates from the decomposition of the accumulated nitrated substances did not meet the criteria for explosive or deflagrating material.

CONCLUSIONS

Thermal and spectroscopic analyses were performed on multiple layers formed when Caustic Side Solvent Extraction (CSSX) solvent was contacted with 16 M or 8 M nitric acid. A rapid (i.e., minutes to hours) chemical reaction occurred between the solvent and 16 M or 8 M nitric acid as evidenced by color changes and the detection of the nitro group in the infrared spectrum of the aged samples. Thermal analysis revealed that the decomposition of the aged mixture does not meet the definition of explosive or deflagrating material. The mixture used in this testing contains a very high concentration of organic to acid compared to that expected for operations in the Analytical Labs, given the expected short operational lifetime for MCU (i.e., 3–5 years), the limited number of samples analyzed, and the low entrainment levels of CSSX solvent in aqueous solutions.

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