

## FUEL-OXIDIZER MIXTURES: THEIR STABILITIES AND BURN CHARACTERISTICS

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*A survey of the stability and performance of 11 solid oxidizers and eight fuels was performed by differential scanning calorimetry (DSC), simultaneous differential thermolysis (SDT), and hot-wire ignition. Fuels used in the study were sugars and alcohols as well as sulfur and charcoal; all but charcoal melted below 200°C. The goal of the study was to determine whether the oxidizer or fuel controls the essential properties of the mixture. Several general observations were made: (1) There was wide variability in DSC results, even using the same batch of a mixture. (2) SDT traces often differed markedly from those of DSC. (3) At 50 wt % sugar, decomposition generally occurred as soon as the fuel melted. (4) With only 20 wt % sucrose, many of the oxidizer/fuel mixtures still exhibited the first exotherm immediately after the melt of the fuel. This behavior was so general that we have classified the decomposition of the fuel-oxidizer mixtures as fuel or oxidizer controlled. Oxidizer-controlled mixtures were those made with  $\text{KClO}_4$ ,  $\text{KNO}_3$ , or  $\text{NH}_4\text{ClO}_4$ ; they did not exhibit substantial exotherms until the oxidizer underwent a phase change or decomposition. A fuel-controlled mixture meant decomposition of the mixture ensued immediately after the fuel melted. This was the case with  $\text{KIO}_4$ ,  $\text{KIO}_3$ ,  $\text{KBrO}_3$ ,  $\text{KMnO}_4$ ,  $\text{KNO}_2$ , and  $\text{KClO}_3$ . Fuel-controlled oxidizer/fuel mixes exhibited lower decomposition temperatures than oxidizer-controlled mixtures.*

**KEY WORDS:** *explosives, FOX, inorganic oxidizers, thermal stability, burn*

### 1. INTRODUCTION

Inorganic oxidizers find applications ranging from oxygen sources to sources of energy and propulsion. Examples include ammonium perchlorate with hydroxy-terminated polybutadiene for rocket fuel and ammonium nitrate with fuel oil for commercial mining. Many of these formulations have also found illicit use [1]. Herein, a number of solid oxidizers, with varying oxidizing power, were tested on a laboratory scale in mixtures with a variety of fuels. The objective was to assess their hazard and threat potential and to allow assessment of the usefulness of small-scale tests. Many of the oxidizers were oxy halide salts. These anions, with the highly oxidized central atoms, tend to be useful oxidizing agents which work most effectively in acidic solutions. The potassium, rather than the sodium, salts were used, since formulations with potassium cation tend to be

less hygroscopic than those of sodium. The ammonium salts have different chemical behavior than potassium salts of the same anion because they carry and use, if required, their own fuel. The choice of fuels, like oxidizers, was limited to solids: polyalcohols, sulfur, and charcoal. The solid alcohols, some classed as sugars, melt at relatively low temperatures. Most fuels were combined with the oxidizers at a 50/50 wt % level. These fuel-rich mixtures are typical for pyrotechnic formulations. In addition, oxidizer/sucrose 80/20 mixtures were examined and compared to the 50/50 mixtures. For purposes of comparison, one nonalcohol, but low-melting fuel, sulfur, and a nonmelting fuel, charcoal, were examined.

## 2. EXPERIMENTAL

Eleven oxidizers and eight fuels were employed. All materials were reagent grade with the exception of the charcoal, which was purchased locally. The oxidizer/fuel mixtures were examined fuel rich at 50/50 wt % and closer to stoichiometric at 80/20 wt %. Actual stoichiometric ratios are shown in Table 1. Individual components with larger particle sizes (i.e., sugars and most oxidizers) were ground with a mortar and pestle prior to mixing. Those materials that were already fine powders, such as sulfur, were

**TABLE 1:** Calculated stoichiometric weight percent of oxidizer with specified fuels

	Stoichiometric mixtures ( wt % oxidizer)					
	KIO <sub>4</sub>	KMnO <sub>4</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	KCr <sub>2</sub> O <sub>7</sub>	KIO <sub>3</sub>
Sucrose	80.1	81.6	79.6	74.1	87.3	83.3
Lactose	80.1	81.6	79.6	74.1	87.3	83.3
Fructose	79.3	80.8	78.8	73.1	86.7	82.6
Glucose	79.3	80.8	78.8	73.1	86.7	82.6
PE	83.5	84.8	83.1	78.3	89.6	86.3
ET	80.9	82.3	80.4	75.1	87.8	84.0
Sulfur	78.2	79.8	77.6	71.8	85.9	81.6
Charcoal	90.5	91.3	90.3	87.2	94.2	92.2
	KClO <sub>4</sub>	KNO <sub>3</sub>	KNO <sub>2</sub>	NH <sub>4</sub> ClO <sub>4</sub>	NH <sub>4</sub> NO <sub>3</sub>	
Sucrose	70.8	73.9	79.9	76.7	84.9	
Lactose	70.8	73.9	79.9	76.7	84.9	
Fructose	69.8	72.9	79.1	75.8	84.2	
Glucose	69.8	72.9	79.1	75.8	84.2	
PE	75.3	78.1	83.3	80.6	87.6	
ET	71.9	74.9	80.7	77.6	85.5	
Sulfur	68.4	71.6	78.0	74.6	83.3	
Charcoal	85.2	87.1	90.4	88.7	93.0	

used as received. Materials used to make the 80:20 sucrose mixtures were sieved to 50–100 mesh. Mixtures were generated by either gently stirring the fuel and oxidizer together in a ceramic dish with a wooden stick (earlier mixes), or by mixing them in a Resodyn LabRAM acoustic mixer for 2 min (50% intensity, frequency set to automatic). Mixture sizes ranged from 100 mg to 1 g, depending on the analyses to be performed.

A TA Q100 differential scanning calorimeter (DSC) was used, and samples were scanned at 20°/min. Samples of about 0.25 mg were flame sealed in glass capillaries (borosilicate 0.06 in. ID, 0.11 in. OD) held on a liquid-nitrogen-cooled metal post to ensure that decomposition did not occur during the sample preparation process. To ensure the integrity of the capillary sealing (i.e., no leaks), capillaries were weighed before and after DSC analysis. A TA Instruments Q600 simultaneous TGA/DSC (SDT) was used with unsealed samples held in ceramic crucibles. Empty crucibles were placed in the SDT, where they were weighed by the internal balance and about 5 mg of sample was added. Ceramic caps (i.e., not tightly sealed) were placed on the crucibles for samples which might eject material or on highly volatile samples, e.g., sulfur mixtures. The SDT was used because of its extended temperature range (1000°C vs 450°C for DSC). However, the thermograms obtained with sealed DSC did not perfectly match those observed with the unsealed ceramic pans used on SDT. The open pans allowed for the sample to volatilize as compared to the sealed scenario, where there is considerable pressure buildup. Differences for SDT included somewhat smaller exotherms, some smaller exotherms became endotherms, and larger exotherms were sometimes split by an endotherm. For this reason the sealed DSC tube results were reported for temperatures below 450°C; if temperatures above that are reported, they are SDT results.

Samples were usually run in triplicate, but where marked variations in the thermograms were apparent, up to seven samples were run. Because multiple endotherms and exotherms were often observed in the DSC and SDT traces and because many of the exotherms covered a wide temperature range (in a few cases up to 100°C), the major exotherm of a trace is usually reported with the initial temperature at which a deviation from baseline was visually detected followed by the temperature(s) at which “peak maxima” were observed, with the highest in bold, followed by the energy density of the mixture (J/g) calculated from the peak area using baselines established by the operator (Table 3).

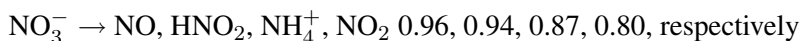
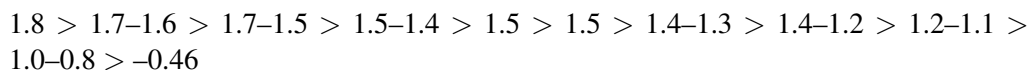
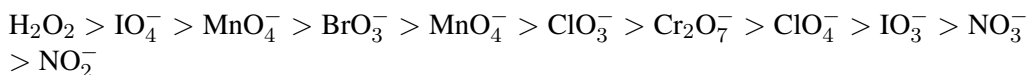
For burn tests the oxidizers and sucrose were dried overnight in a vacuum oven at 50°C and then ground and sieved to 50–100 mesh. Pyrotechnic-grade (median particle size 23  $\mu\text{m}$ ) aluminum powder (Obron) was used. Samples were mixed with a Resodyn LabRAM acoustic mixer at 50% intensity for 2 min. Approximately 0.25 g samples were placed in a pile on a ceramic plate over a loop of 22 gage nichrome wire (30 cm long for power requirements of 150 W) attached to a variable autotransformer (set to 20 V) with a 25 amp internal fuse for the burn. Light output was recorded with a DET36A detector (Thor Labs) and recorded using a National Instruments USB-6210 data acquisition module. Light data was recorded at 10–100 kHz by measuring voltage

across a 350 ohm resistor. The detector was unfiltered for mixtures producing low levels of light (e.g. 80/20 or 50/50 oxidizer/sucrose). To resolve the brightest events (e.g. 80/20 oxidizer/aluminum powder), a 90% neutral density filter (ND10A, optical density of 1.0) was applied behind an iris (6.33 mm diameter opening, Iris SM1D12). The data acquisition card was set to a sampling rate of at least 10 kHz, with a pretrigger of 50–100 ms.

### 3. RESULTS AND DISCUSSION

#### 3.1 Neat Species

Oxidizers were restricted to solids of various oxidizing power. Oxidizing power itself is variously rated. Intrinsic oxidizing ability, given by standard reduction potential (1 M aq solution against H<sub>2</sub> as zero) in volts, is a meaningful approach to quantifying oxidizing power. This is given below starting with the species having the most positive potential, noting that actual potentials depend on the pH of solutions and final products:



An alternative approach to rating oxidizing power is a burn test. The U.N. Manual of Tests and Criteria rates an oxidizer by comparing its burn rate in an admixture with cellulose (2:3 and 3:7 ratios) to mixtures of potassium bromate/cellulose [2]. In our burn tests 250 mg, instead of 30 g, and sucrose or aluminum powder were used instead of cellulose. Fuel-oxidizer burn rates are shown in Table 2.

Thermal stability was assessed by the temperature at peak maximum of the DSC exotherm. The higher the exotherm temperature, the more thermally stable the species. Some salts decomposed with an exclusively endothermic response (Table 3). Among salts releasing heat (i.e. exothermic response), the amount of heat varied dramatically from more than 1000 J/g for mixtures of ammonium salts, which can undergo self-oxidation, to a few hundred joules per gram for other mixtures. The thermal traces of the oxidizers alone were not simple. They included phase change(s), decompositions, and heats of fusion (i.e. melts) of the decomposition product. Some salts  $\text{EO}_4^-$  underwent intraconversion with a related oxide  $\text{EO}_3^-$ , E = Cl or I. In the case of the periodate/iodate pair, periodate decomposed to iodate at about 330°C and thereafter their thermograms were identical [3–7].

Ammonium perchlorate (AP,  $\text{NH}_4\text{ClO}_4$ ) alone did not melt but exhibited an endotherm around 245°C (~70 J/g) as a result of an orthorhombic-to-cubic phase change.

**TABLE 2:** Burn time (seconds) of a 4:1 oxidizer:sucrose mix

Oxidizer	KIO <sub>4</sub>	KMnO <sub>4</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> ClO <sub>4</sub>	KClO <sub>4</sub>	KIO <sub>3</sub>	KNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	KNO <sub>2</sub>
Anion potential 1 M aq. H <sub>2</sub> O V	1.7-1.6	1.7-1.5	1.5-1.4	1.5	1.4-1.3		1.4-1.2	1.2-1.1	1.0-0.8		-0.46
Wt % oxygen in oxidizer	28%	25%	29%	39%	16%	34%	46%	22%	40%	20%	28%
Decomp °C 8/2 oxidizer/sucrose	187	236	186	180	231	484	540	182	396	176	212
J/g heat released	1681	1741	1511	3195	157	1342	735	939	1108	2084	1777
Burn test 8:2 oxidizer:Al	KIO <sub>4</sub>	KMnO <sub>4</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> ClO <sub>4</sub>	KClO <sub>4</sub>	KIO <sub>3</sub>	KNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	KNO <sub>2</sub>
Avg. burn time by eye (s)	Too fast	Too fast	Too fast	Too fast	Too fast	4.3	Too fast	7.5	3.8	18.2	2.5
Std. dev.	Too fast	Too fast	Too fast	Too fast	Too fast	1.0	Too fast	2.1	0.7	1.6	0.6
Avg. peak light signal (mV)	2564	2360	1113	1129	140	144	2736	-	-	-	-
Std. dev.	232	297	437	286	54	73	11	-	-	-	-
Notes	Bright flash	Bright flash	Bright flash	Bright flash	Bright flash	Bright flash, strobos	Bright flash	Bubbled	Bubbled	Bubbled	Bubbled
Burn test 8:2 oxidizer:sucrose	KIO <sub>4</sub>	KMnO <sub>4</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> ClO <sub>4</sub>	KClO <sub>4</sub>	KIO <sub>3</sub>	KNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	KNO <sub>2</sub>
Avg. burn time by eye (s)	Too fast	1.9	Too fast	1.0	4.9	4.6	2.5	1.6	2.5	18.1	1.3
Std. dev		0.2		0.4	1.7	0.8	0.4	0.4	0.7	2.7	0.3
Avg. peak light signal (mV)	56	25	346	104	-	3	11	-	-	-	32

TABLE 2: Continued

Oxidizer	KIO <sub>4</sub>	KMnO <sub>4</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> ClO <sub>4</sub>	KClO <sub>4</sub>	KIO <sub>3</sub>	KNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	KNO <sub>2</sub>
Std. dev.	23	6	98	43	–	1	4	–	–	–	12
Notes	Purple flickering	Orange flame	Purple flame	Purple flame	Charring, no flame	Yellow flame	Purple flame	Charring, no flame	Charring, no flame	Dim yellow flame	Yellow flame
Burn test 5:5 oxidizer:sucrose	KIO <sub>4</sub>	KMnO <sub>4</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> ClO <sub>4</sub>	KClO <sub>4</sub>	KIO <sub>3</sub>	KNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	KNO <sub>2</sub>
Avg. burn time by eye (s)	3.1	10.4	Too fast	2.6	15.9	9.2	8.1	9.0	0.9	21.4	2.6
Std. dev.	0.5	2.1	Too fast	0.8	1.7	1.2	1.1	4.2	0.1	4.8	1.1
Avg. peak light signal (mV)	–	8	430	128	–	10	58	–	43	–	43
Std. dev.	–	7	164	41	–	2	13	–	13	–	13
Notes	No light, black snake	Dim yellow flame	Purple flame	Purple flame	Dim yellow flame	Dim yellow flame	Dim yellow flame	Dim yellow flame	Dim yellow flame	No light, black snake	Dim yellow flame
Burn test 8:2 oxidizer:benzoic acid	KIO <sub>4</sub>	KMnO <sub>4</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	NH <sub>4</sub> ClO <sub>4</sub>	KClO <sub>4</sub>	KIO <sub>3</sub>	KNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	KNO <sub>2</sub>
Avg. burn time by eye (s)	1.6	3.0	Too fast	4.4	16.0	6.3	4.5	4.9	4.5	28.7	2.1
Std. dev.	0.5	0.8	Too fast	1.7	1.6	1.0	0.6	1.2	1.8	6.2	0.5
Avg. peak light signal (mV)	1413	147	2228	762	26	226	737	221	91	14	160
Std. dev.	331	22	228	104	8	45	304	35	33	4	88
Notes	Bright flash	Orange flame	Bright flash	Br yellow flame	Yellow flame	Br yellow flame	White flame	White flickering	Orange flame	Yellow flickering	Orange flame

**TABLE 3:** Temperature endotherms & exotherms for DSC & SDT at 20°/min (heat release J/g)

	KIO <sub>4</sub>		KMnO <sub>4</sub>		KBrO <sub>3</sub>	
	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm
<b>Phase change</b>						
<b>Melt</b>			SDT only			
<b>Melt KX</b>				240 lit start peak	413(60)	
<b>Decompose</b>				541(59)	729(488)	
<b>Sucrose</b>			334-350(85)	305(145)		446(227)
	173-190-201 (148), 238(26)	257-297-334 (206)	65 150(30), 675 (25)	65a 153-171(1698), 293-348(198) sdt, 442(328) sdt	91 180(66), 730(22)	91 184-208-236 (1298), 374(65) sdt
<b>Sucrose 20%</b>			76 675(32)	75 155-167-187 (1681), 297(24) sdt, 349(183), 441-460 (469) sdt	79 180(66), 792	79 170-178-186 (1511) dsc, 372(604) sdt
<b>Lactose</b>	151(132), 208(68)	282-299(419)				
<b>Fructose</b>	88-128-162 (263)	268(233)	66 675(24)	66 132(780), 348 (37), 434(230)	92 115(55), 730(11)	92 200(1421), 372(372) sdt
<b>Glucose</b>	165(198), 233(73)	305(333)				
<b>Pentae-rythritol</b>	191(311), 263 (32), 350(81)					
<b>Erythritol</b>	124(385), 330(547) bp		67a 600(4), 662(24)	67a 137-188, 244(1059), 351(7), 435(28)	93 190(50), 730(46)	93 211-223-239-260-304(1371), 600(2000)
<b>Surfur</b>	108-115-121 (70), 180(8), 315		89 114(17), 578(2)	89 236-262-284-298(1269)		
<b>Charcoal</b>		150				
				KIO <sub>4</sub>		KBrO <sub>3</sub>

TABLE 3: Continued

	KClO <sub>3</sub>		K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		NH <sub>4</sub> ClO <sub>4</sub>		KClO <sub>4</sub>	
	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm
Phase change					248(62)		307(85)	
Melt	58(116)		398				613(115)	
Melt KX	767(177)		757(10)		767(177)		757(10)	653(266)
Decompose		417(9), 584-619(446)				404(1081)		
Sucrose		14 153-164-215-249-256(1955)	95 187(13)	95 244(83), 403(15), 491(32)	28 165(66), 246(24), 759(79)	28 175-185-209(181), 266-280-340-424(1843)	26 181(66), 307(36), 765(7)	26 280(142), 427-494(1206) sdt
Sucrose 20%	5 766(123)	73, 5 162-180-236(3195), 338(61)	94 193(34)	94 225-244-268(159)	71 173(35), 245(54), 758(6)	71 484(1342) dsc, 318 sdt, 394 sdt	74 187(32), 304(85), 787(170)	need DSC 74 540(735), 620(223)
Lactose	15 150(60)	15 182-200-241-253-270(1684)						
Fructose	17 123(11), 767(29)	17 125-175-242-276(2955)	96 101(50)	96 187(130)	29 118(117), 244(10)	29 180(300), 284-340-420(2285)	27 128(29), 311(45), 767(16)	27 511(931)
Glucose	16 155(19)	16 158-175, 240-283(2193)						
Pentae-rythritol	31 191(176), 767(91)	31 209-237-265(2111), 617(45)						
Erythritol	30b 120(260)	30b 195-216-259-280(2339)	97 193(24), 398(123)	97 404(89)	44 108(45), 246(53),	44 262-298-340-438-452(3196)	45 118(200), 306(18), 768(52)	45 329-355(438), 503-575-644(213)
Surfur	38a 115(33), 317(7), 440(17)	38a 142-180(829)			85 114(37), 245(25), 670(11)	85 389-421(1493)	84 115, 120(54), 307(36), 765(14)	84 424-470-486(1384), 597(154)
Charcoal	42	42 334(1541)	98 395(23)	98 401(61)	69 244(20)	69 344(2000)	54, 70 307(43), 766(14)	70 449-524(1100)
		KClO <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		NH <sub>4</sub> ClO <sub>4</sub>		KClO <sub>4</sub>	



TABLE 3: Continued

	KIO <sub>3</sub>		KNO <sub>3</sub>		NH <sub>4</sub> NO <sub>3</sub>		KNO <sub>2</sub>	
	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm
Phase change		nothing in DSC	132(53), 222(3)		55(22), 130(40)		45(13)	
Melt	553d(609)		330(29)		167		424(82)	
Melt KX	680(75)							
Decompose	831-900(275)		702(433)				517(2), 903(17)	930(176)
Sucrose	62 152(19), 678(8)	62 156-187 (1736), 438(137) sdt	18 137(22), 181(73), 219(14)	18 219-265 (298), 359-393 (400 or 1269)	22 54(16), 127(15)	22 147-176 (2627), 296(513)	55 192(57)	55 212-239-290(1618)
Sucrose 20%	77 160(39)	77 163-182(939) dsc, 434(207) sdt	72 131(45), 173(20)	72 381-396-413-453(1108)	68 56(14), 129(33)	68 151-176, 202(2084), 283-295-333(1010)	78 172(41), 940(21)	78 177-212-222-251(1777), 323-333(65)
Lactose			19 132(9), 151(70), 212(9)	19 271(300), 379-394(800)	23 55(10), 107(110)	23 160-182-209, 221 (1493), 311(183)		
Fructose	63 123(27), 678(10)	63 128-156 (1491), 430(117)	21 122(72)	21 230-314-380 (244), 409(550)	25a 55(15), 130(80)	25a 150-170(3475), 336(607)		56 136-170-218 (944)
Glucose			20 133-152-165 (140)	20 271-305 (370), 392(414)	24 54(11), 107(90)	24 153-188(2400), 309(318)		
Pentae-rythritol			(23), 190(139), 354(164), 687(849)	440, 470(1467), 765, 842, 940	33 54(13), 126 (38), 175(9)	33 242-265(2008)		
Erythritol	64 123(119), 608(2), 668(15)	64 178(931)	34 113(125), 130(32)	34 298(30), 416(2695)	35 86(59), 119(11)	35 255-261(1653)	57 116(43)	57 250-318-357 (1041)
Surfur	88 114, 119(28)	88 270-363-400(2411)	40a 115, 119, 131(65), 189(12)	40a 300-327-420(1092)	39 116(40)	39 198-217(2379)		87 251-294-310(1962)
Charcoal			43 129(22), 332(47)	43 461(2182)		41 221(1472)		
		KIO <sub>3</sub>	KNO <sub>3</sub>		NH <sub>4</sub> NO <sub>3</sub>		KNO <sub>2</sub>	

[Ammonium chlorate is thermally unstable and has been reported to spontaneously ignite at temperatures as low as 100°C [8]. For this reason it was not used in this study.] Continued heating of AP in sealed DSC ampules resulted in a single exotherm which began around 350°C and reached a maximum at about 400°C (~1300 J/g). The SDT results appeared quite different. Immediately after the 245°C phase change, a small exotherm (~360 J/g) at ~318°C was observed with a second endotherm centered around 435°C following it (Fig. 1). This apparent difference in AP behavior has been explained by the sublimation of AP above 350°C competing with its decomposition. In the sealed DSC ampule, AP did not sublime. It has been reported that the competition between AP sublimation and AP decomposition was dramatically affected by pressure [9]. [As heating of the open pan in the SDT was continued, a small endotherm at 757°C was observed, the melt of KCl.]

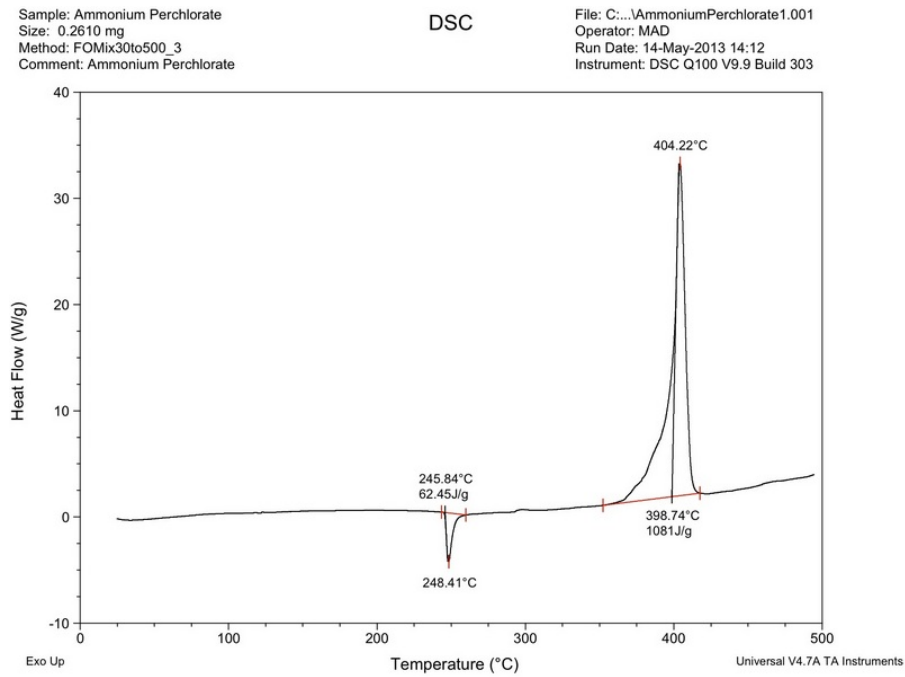
An advantage of the SDT thermal analysis was that it allowed scanning to higher temperatures. Since the crucibles were not sealed, thermal traces differed markedly from sealed DSC thermal analysis. For example, the exotherm in the ammonium nitrate (AN,  $\text{NH}_4\text{NO}_3$ ) thermal trace at 316°C in SDT became an endotherm at 292°C due to the volatilization of the AN. This same observation was made with a number of compounds and formulations. Sulfur, in the open pans, exhibited an exotherm at around 400°C. This was evidently a reaction with oxygen in air, since no exotherm was observed when the samples were scanned under nitrogen.

The fuels, mostly alcohols, melted below 200°C; only charcoal did not exhibit a melt. The monosaccharides, glucose and fructose, and the disaccharides, sucrose (glucose and fructose) and lactose (glucose and galactose), were examined in mixture with 11 oxidizers. The disaccharides and glucose exhibited an endotherm at around 150–176°C, while for fructose the endotherm was earlier at 128°C. Pentaerythritol and erythritol not only had melting points in the temperature range of the other sugars (191°C and 124°C, respectively), but both of them boiled before 300°C. These endothermic events ensured that thermal scans in open pans would be markedly different than in sealed pans. In addition to solid alcohols, sulfur and charcoal were used as fuels. Although sulfur had a low-melting endotherm, charcoal did not. Upon heating in air, sulfur exhibited an exotherm attributed to oxidation.

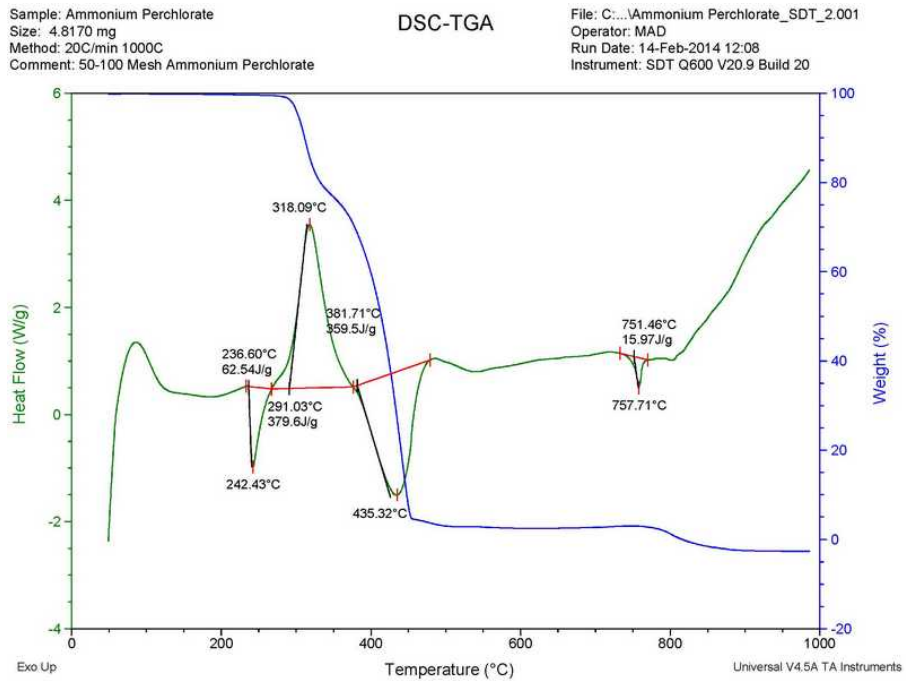
## 3.2 Oxidizer/Fuel Mixtures

### 3.2.1 Periodate

A number of kinetic and mechanistic studies have been done on the oxidizing power of periodate [10, 11]. For example, it has been reported that  $\text{KIO}_4$  oxidized glucose to formaldehyde and formic acid through a cyclic diester of periodic acid. The DSC thermograms of  $\text{KIO}_4$  mixed with either 20 or 50 wt % sucrose were similar [cf. Figs. 2(a) and 3(a)]. Immediately after the melt of sucrose, a single large exotherm was observed.

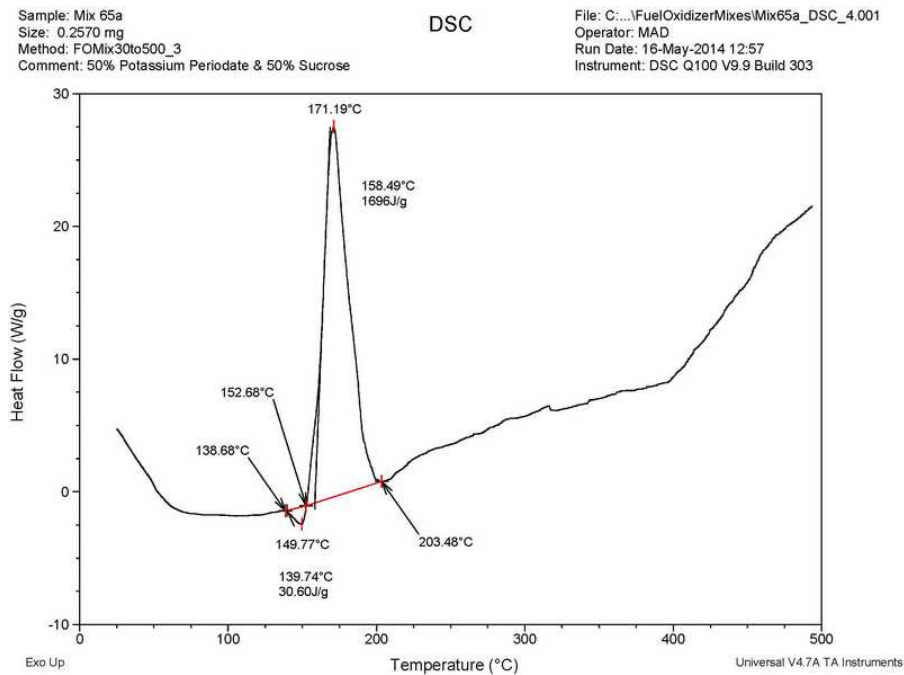


(a)

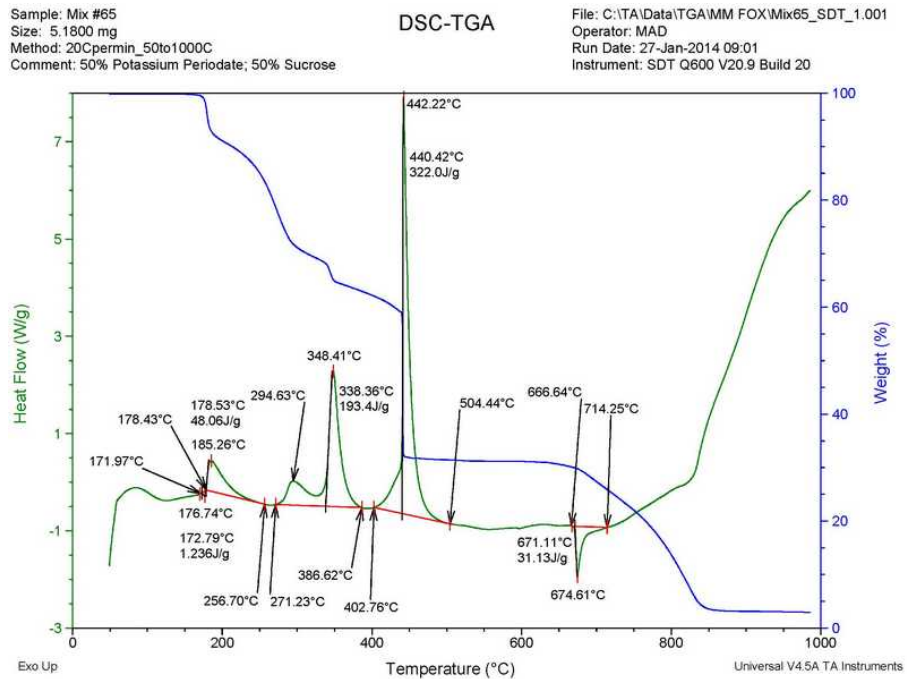


(b)

**FIG. 1: Ammonium perchlorate DSC vs SDT.**

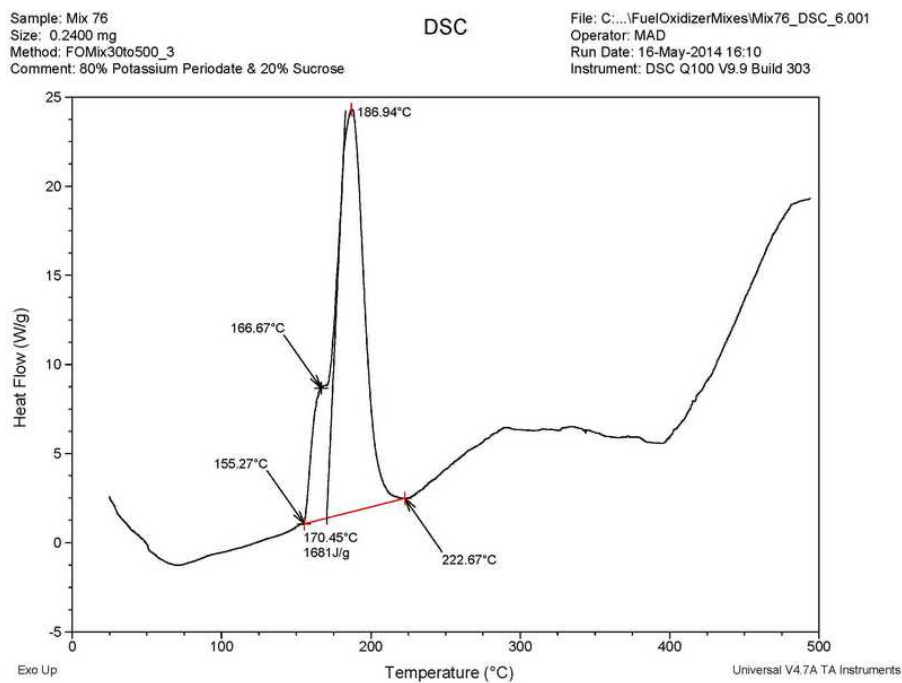


(a)

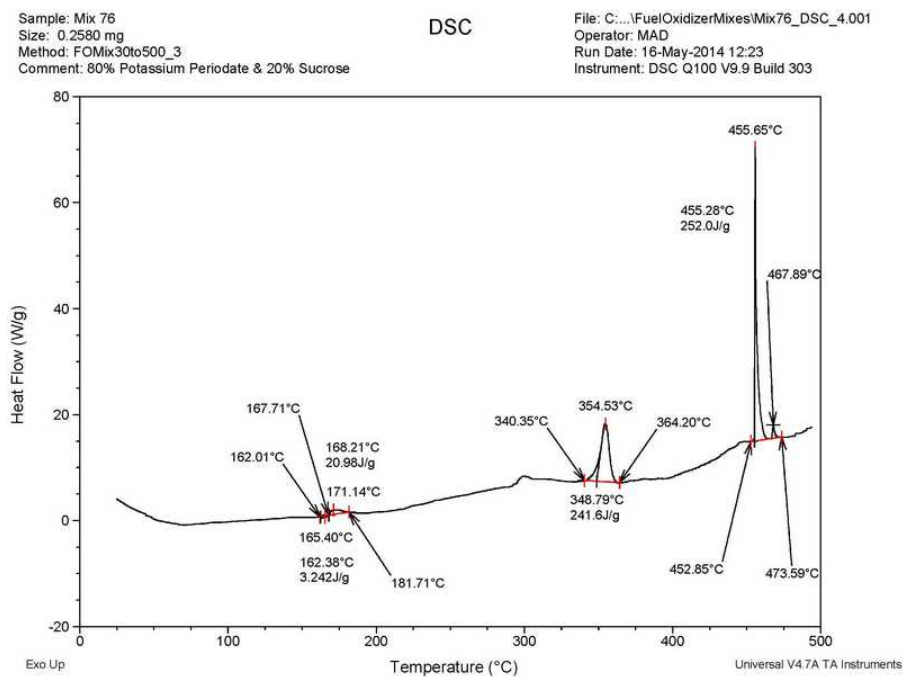


(b)

**FIG. 2:**  $\text{KIO}_4 + 50\%$  sucrose (mix 65)—DSC vs SDT.



(a)



(b)

**FIG. 3:**  $\text{KIO}_4 + 20\%$  sucrose (mix 76)—2 DSC traces.

The SDT of the same mixtures had a different appearance, with a small exotherm immediately after the sucrose melted and additional exotherms around 293°C and 348°C, with a sharp exotherm at 442°C [Fig. 2(b)]. Figure 3(b), which was taken from the same batch as Fig. 3(a), shows the occasional variability encountered in thermal scans. This one may be a result of a leak with partial loss of the fuel component. With 50 wt % fructose or erythritol, the exotherm also began immediately after the melt of the fuel, but the melt came at lower temperatures for fructose (~103°C) or for erythritol (~121°C). Sulfur melted at 115°C and exhibited another slight endotherm at around 180°C. An exothermic decomposition of the periodate/sulfur mix began at about 235°C and rose to a maximum at around 300°C. Figure 4 shows both the DSC and SDT of this event.

### 3.2.2 Iodate

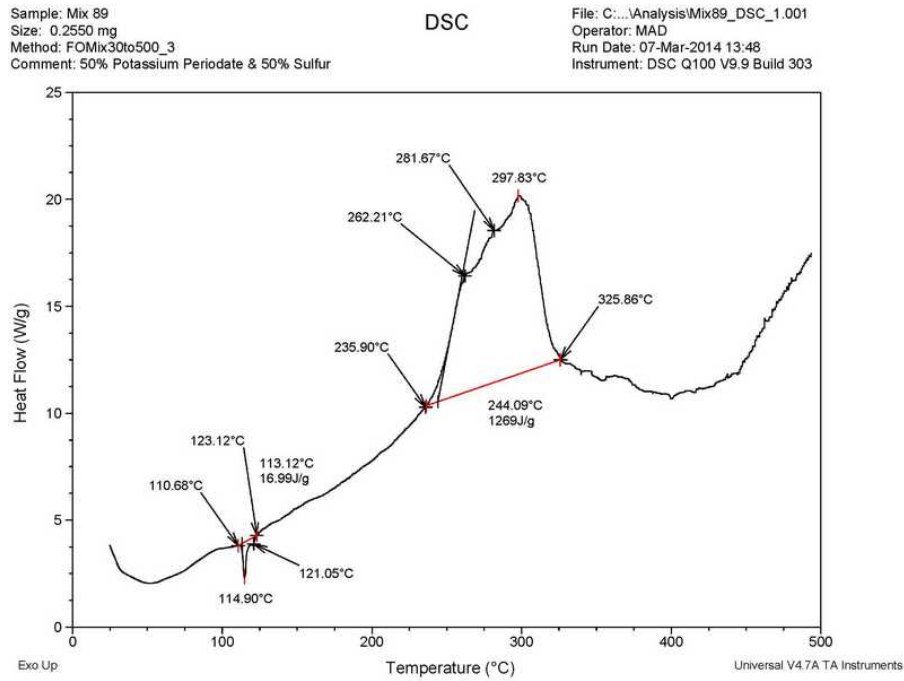
The DSC thermogram of both the 50/50 and 80/20  $\text{KIO}_3$ /sucrose mixtures exhibited large exotherms immediately after the melt of sucrose. Figure 5 shows substantial differences between DSC and SDT. The heat release in the SDT was significantly less than in the DSC (Fig. 5), likely a result of heat of vaporization countering overall heat release. The DSC traces of iodate with 50 wt % fructose or erythritol were similar to those of sucrose, initiating an exothermic reaction immediately after the melt [11].

### 3.2.3 Bromate

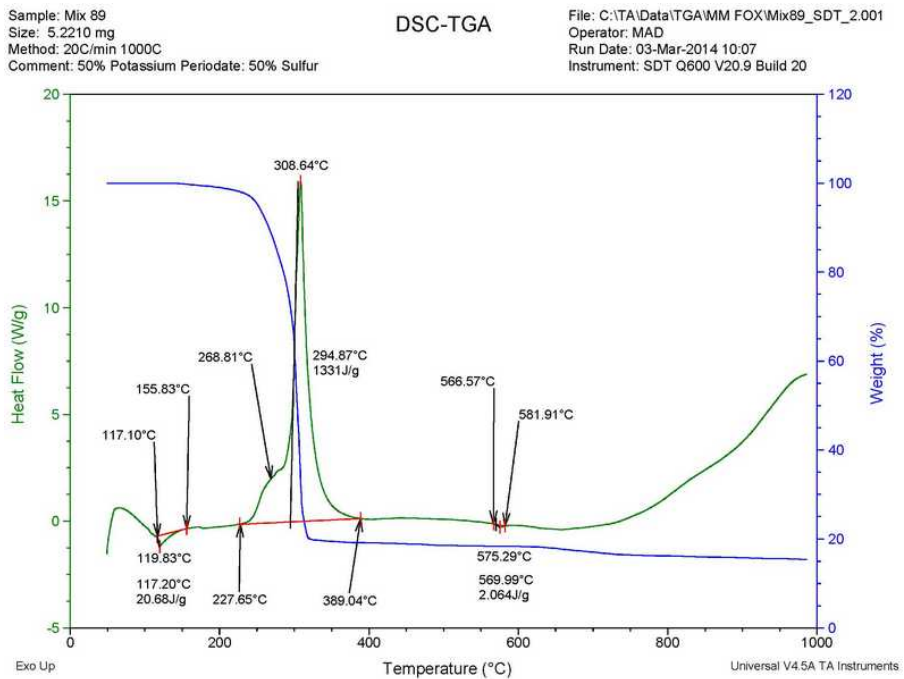
Among the oxo-halides, bromate is among the least studied. Nevertheless, the kinetics of the neat salt  $\text{KBrO}_3$  have been studied by isothermal and dynamic TGA and its oxidation of alcohols reported [12, 13]. The exotherm of  $\text{KBrO}_3$ /sucrose mixtures started immediately after the sugar melted. However, the initial endotherm was not easily observed. It was visible in the mix with 20% sucrose but barely detected in the 50% sucrose mix (Fig. 6). The difference between the DSC and SDT traces was considerable. The DSC exhibited a single exotherm around 206°C; the SDT trace showed that exotherm and a second one at ~374°C. The melt of fructose or erythritol initiated their decomposition with bromate. The same difference between the DSC and the SDT was also observed when the fuel was erythritol—DSC had one exotherm 211–304°C and SDT had at two 234°C and 379°C (Fig. 7).

### 3.2.4 Chlorate

The exotherm of  $\text{KClO}_3$ /sucrose mixes started with a sucrose melt, 180°C. With the 50/50 mix there was only partial separation of exotherms (Fig. 8); the combined heat release totaled about 2000 J/g. Chlorate with 20 wt % sucrose had a similar thermal trace, but the first peak (~180°C) was smaller than the second peak (~230°C). In some traces a second exotherm was observed at ~336°C, the temperature at which chlorate melts

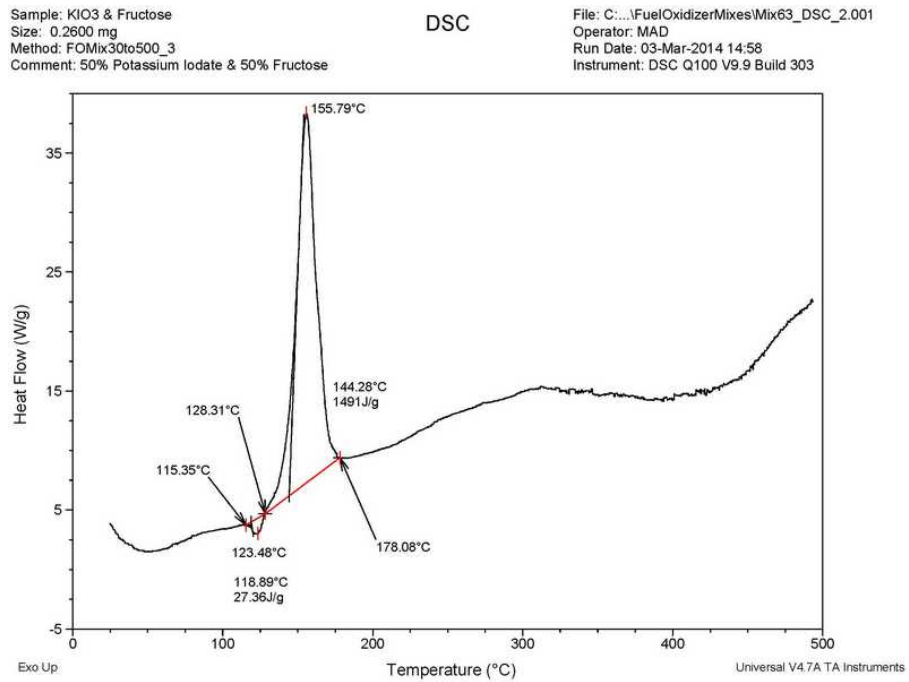


(a)

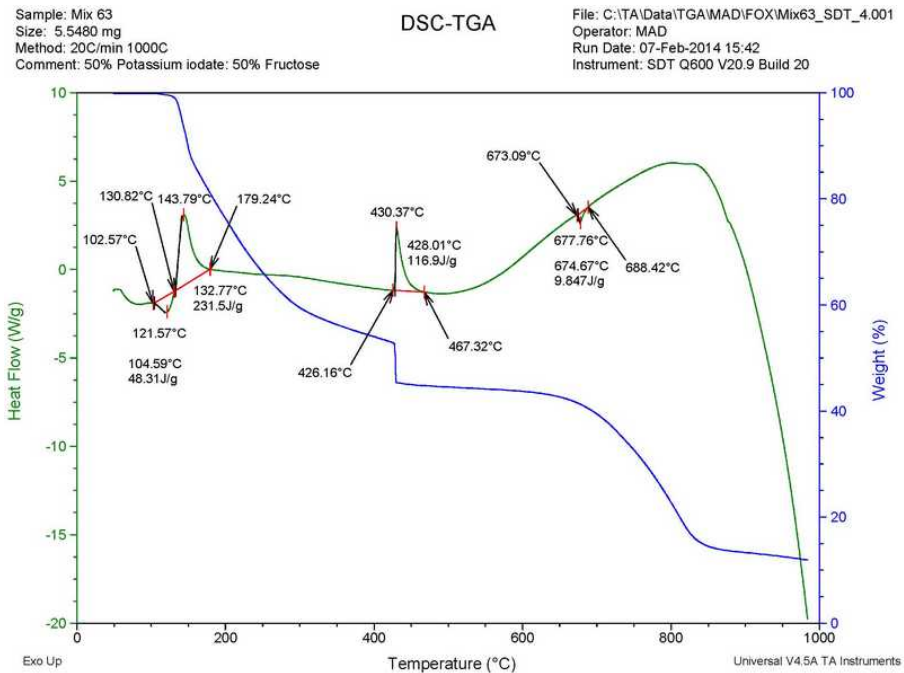


(b)

**FIG. 4:**  $\text{KIO}_4 + 50\%$  sulfur (mix 89)—DSC vs SDTT.



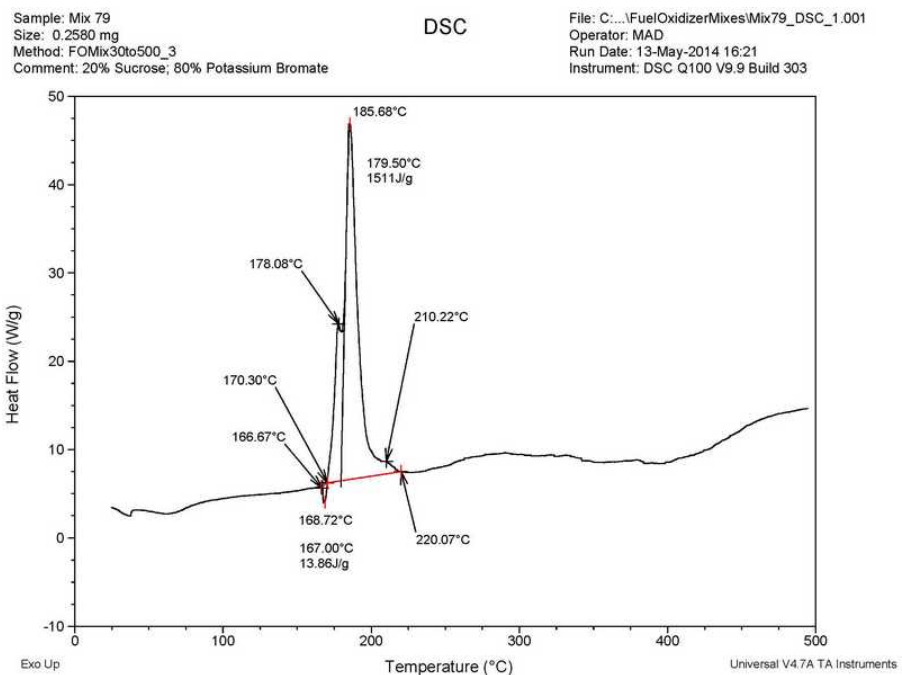
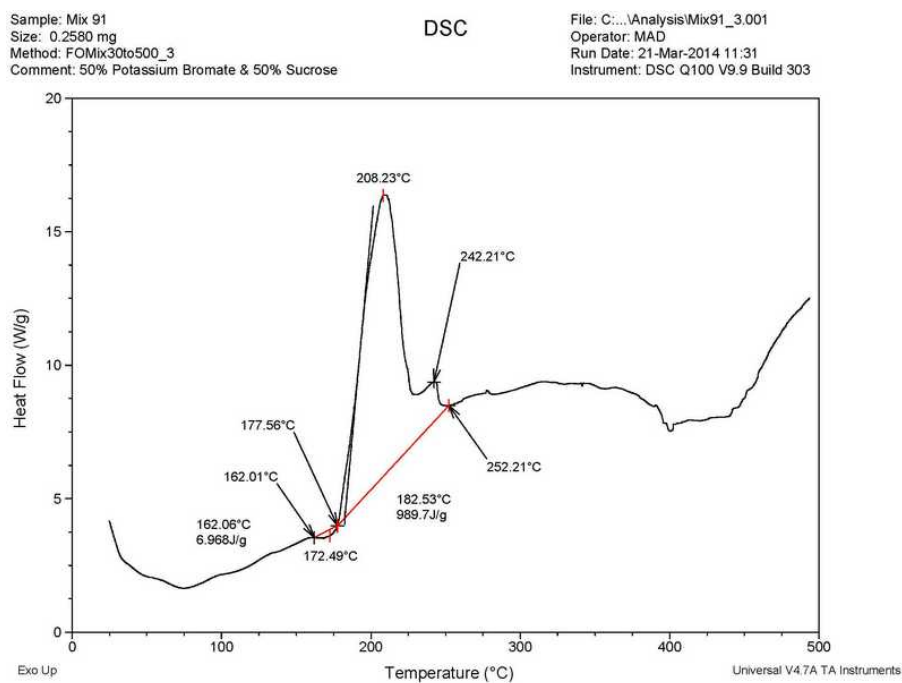
(a)



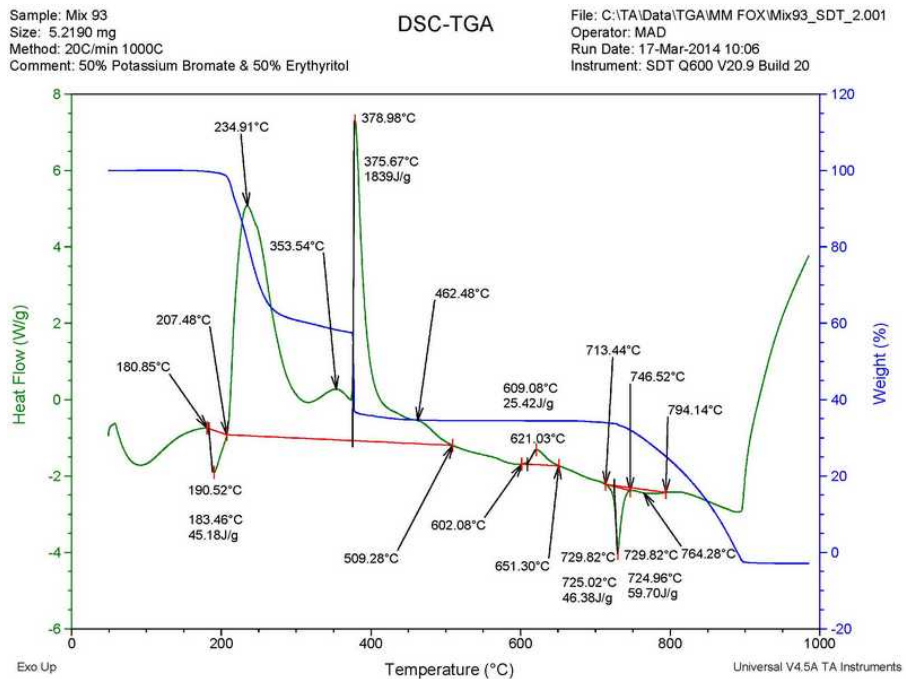
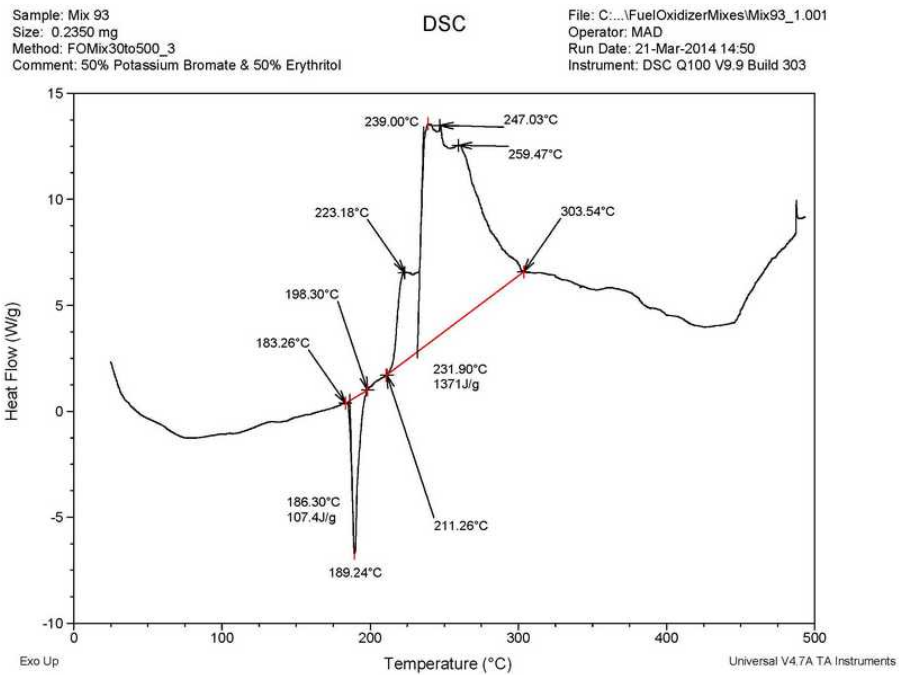
(b)

**FIG. 5:** KIO<sub>3</sub> + 50% fructose (mix 63)—DSC vs SDT.

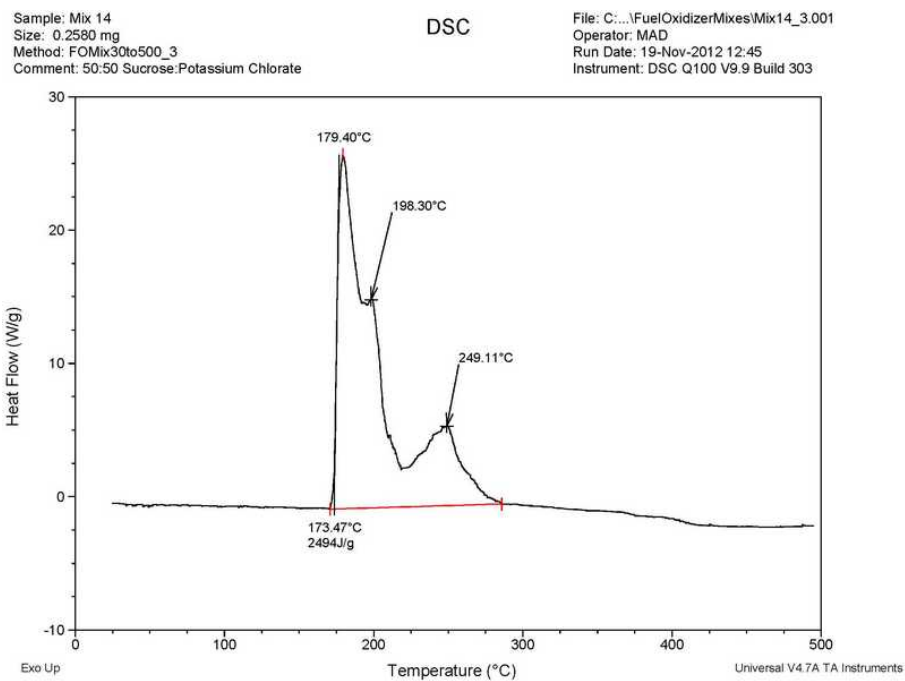
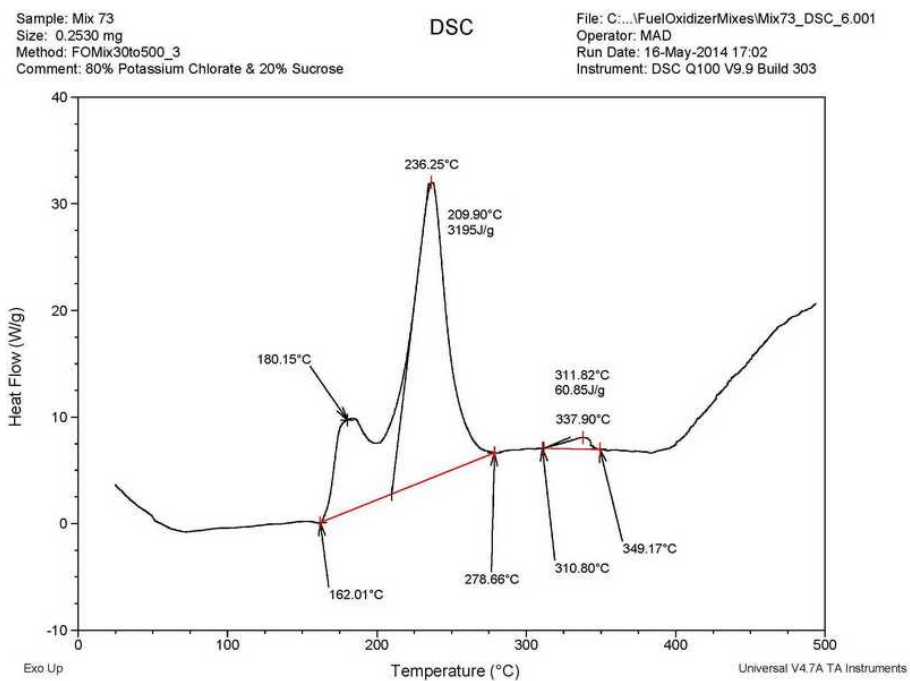




**FIG. 6:**  $\text{KBrO}_3$  + 50% sucrose (mix 91) or 20% sucrose (mix 79).



**FIG. 7:**  $\text{KBrO}_3 + 50\%$  erythritol (30b)—DSC vs SDT.



**FIG. 8:**  $\text{KClO}_3$  + 20% sucrose (mix 73) or 50% sucrose (mix 14).

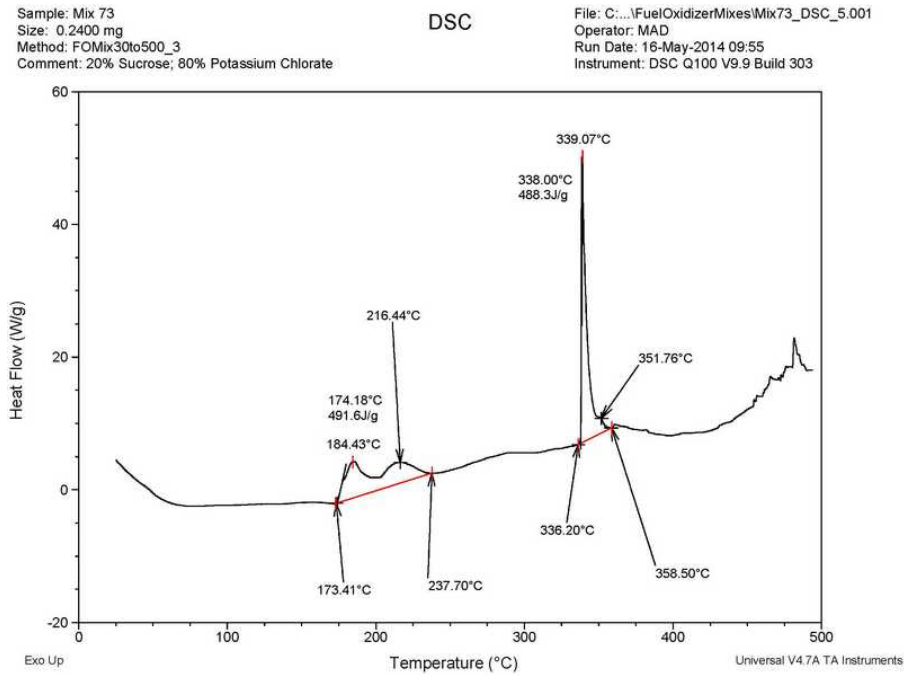
(Fig. 8). Variations in appearance of the DSC thermograms is likely a result of how thoroughly the oxidizer and fuel were mixed. However, the occasional difference among the DSC traces was not nearly as dramatic as the difference between the DSC and SDT thermograms of the same mixture (Fig. 9). A detailed examination of the reaction between  $\text{KClO}_3$  and lactose noted the importance of liquid lactose and its solubilization of the chlorate; it also noted no disproportionation into perchlorate [14, 15]. The 50/50 mix of chlorate with glucose, fructose, or pentaerythritol (PE) also exhibited the exotherm as soon as the sugar melted. Interestingly, although erythritol melted at lower temperature than PE ( $124^\circ\text{C}$  vs  $191^\circ\text{C}$ ), the exothermic reaction between erythritol and  $\text{KClO}_3$  did not begin immediately after the erythritol melt; it was not observed to start until  $195^\circ\text{C}$ , almost the same temperature as the exothermic reaction between PE and  $\text{KClO}_3$ . With the chlorate/charcoal 50/50 mix in a sealed DSC tube, the exotherm was initiated by the melt of  $\text{KClO}_3$ .  $\text{KClO}_3$  with sulfur had one of the lowest temperature exotherms of the oxidizers with sulfur. Sulfur alone had a small endotherm around  $180^\circ\text{C}$ , and the chlorate/sulfur exotherm immediately followed this. This mixture is prone to accidental ignition [16]. In general, low-melting fuels increase sensitivity.

### 3.2.5 Perchlorate

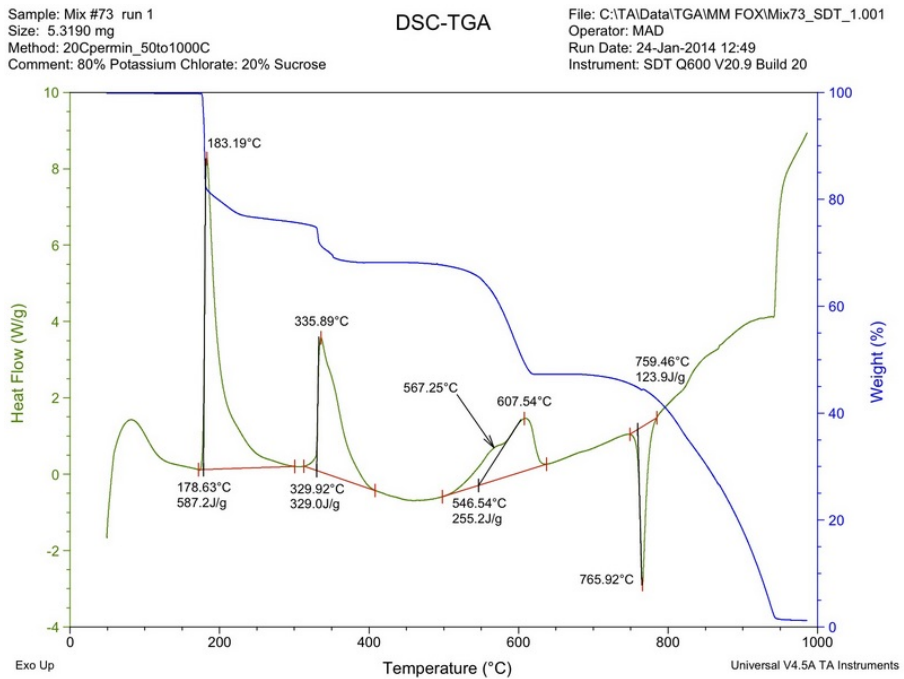
Although there was a slight exothermic “hump” at around  $280^\circ\text{C}$  where sucrose itself decomposed, the main exotherm of the 50/50 sucrose/ $\text{KClO}_4$  mixtures did not occur until almost  $\sim 500^\circ\text{C}$  (Fig. 10) [15]. Neither the melt of sucrose or fructose nor the phase change of the perchlorate ( $\sim 305^\circ\text{C}$ ) instigated the exothermic decomposition of these mixtures, but when erythritol was mixed with  $\text{KClO}_4$ , exothermic decomposition began immediately after  $305^\circ\text{C}$  where  $\text{KClO}_4$  underwent a phase change.

The appearance of the thermograms after the erythritol melt depended on whether the sample was heated open or sealed. Both showed an endotherm for the erythritol melt around  $123^\circ\text{C}$ , but in the open SDT container there was a second endotherm at  $\sim 277^\circ\text{C}$  which blended into the perchlorate phase change at  $305^\circ\text{C}$  (Fig. 11). This extra endotherm was due to the vaporation of the erythritol; thus it was unclear how much fuel remained or whether it was involved in the small exothermic decomposition observed at  $\sim 644^\circ\text{C}$ . In the sealed tubes, the endothermic phase change of  $\text{KClO}_4$  was followed by an exotherm. The melting endotherm of  $\text{KCl}$  was around  $760^\circ\text{C}$ . The volatilization of the fuel in the open-container SDT was also an issue with the perchlorate/sulfur mixtures. Nevertheless, the DSC trace showed several endothermic events for the melt of sulfur polymorphs as well as the melt of  $\text{KClO}_4$ . The exothermic decomposition of the mixture was not observed until almost  $470^\circ\text{C}$ .

The chlorates and perchlorates behaved differently under heating.  $\text{KClO}_3$  with 50 wt % sucrose (mix 14) produced a large exotherm initiated by the melt of sucrose ( $\sim 180^\circ\text{C}$ ) and spanning a large range of temperatures. In contrast,  $\text{KClO}_4$  with 50 wt % sucrose (mix 26) survived the endothermic melt of sucrose and its own phase change ( $307^\circ\text{C}$ ).

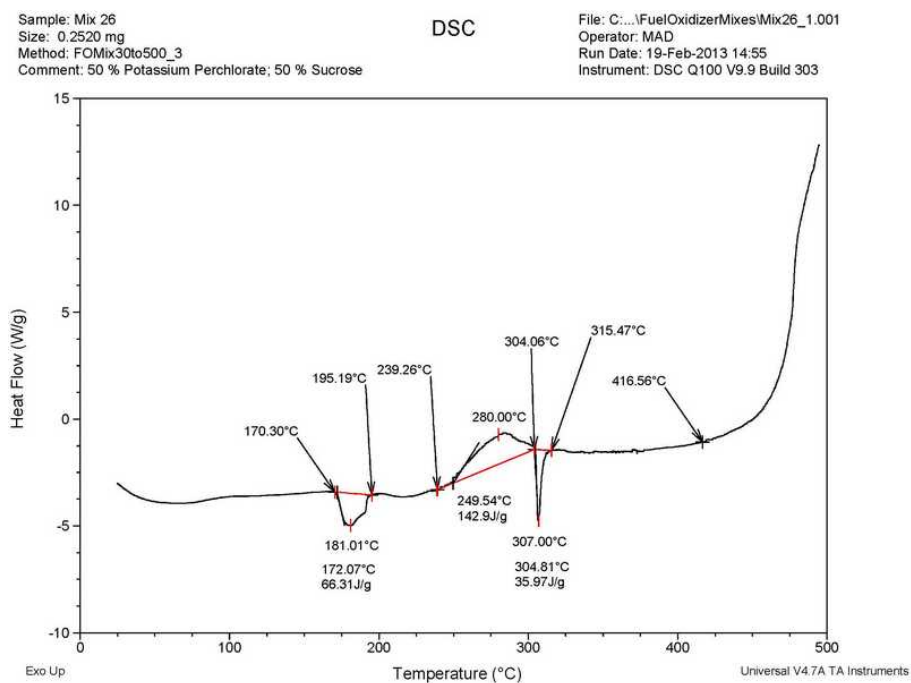


(a)

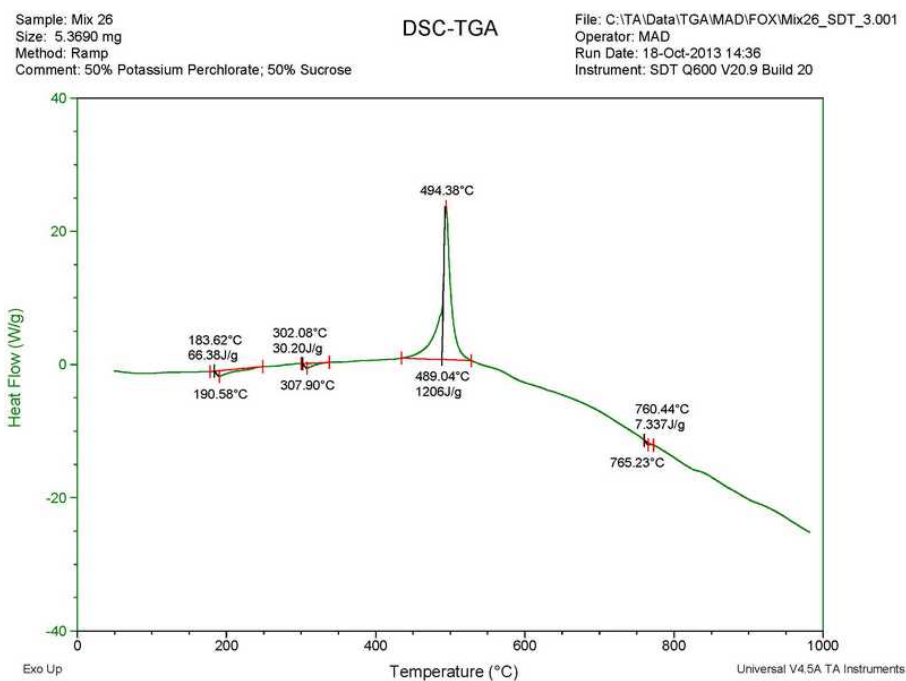


(b)

**FIG. 9:** KClO<sub>3</sub> + 20% sucrose (mix 73)—DSC and SDT.

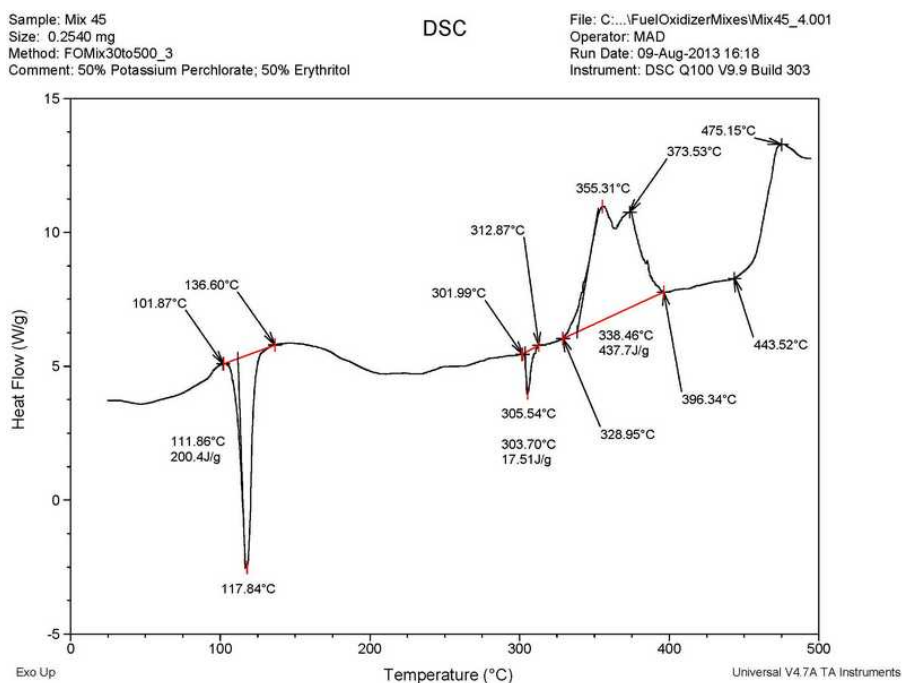


(a)

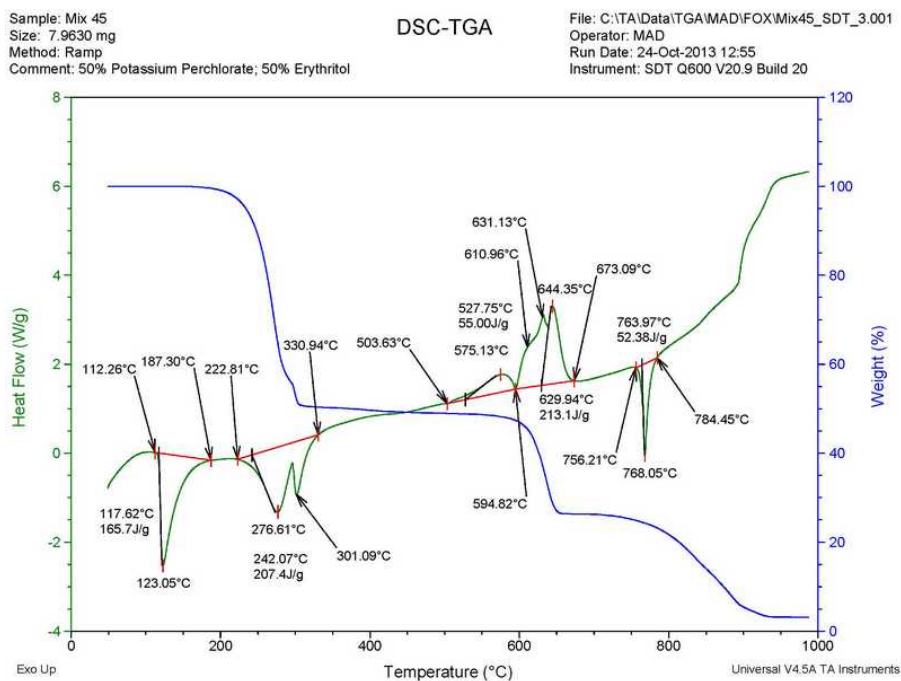


(b)

**FIG. 10:**  $\text{KClO}_4$  + 50% sucrose (mix 26)—DSC and SDT.



(a)



(b)

FIG. 11:  $\text{KClO}_4$  + 50% erythritol (mix 45)—DSC and SDT.

It did not exhibit an exotherm until near its own melting point about 500°C. It exhibited an endotherm at about 760°C, as did  $\text{KClO}_3$ , the melt of KCl. Potassium perchlorate was particularly unaffected by its fuel, although for most fuels an exotherm could be observed above 500°C.

### 3.2.6 Ammonium Perchlorate

$\text{NH}_4\text{ClO}_4$  (AP) with 50 wt % sucrose (mix 28) or fructose (mix 29) began to exothermically decompose immediately after the sugar melted, but the heat released was small, only a few hundred joules per gram; this is likely partial decomposition of the sugar. Not until after an endotherm around 246°C, the phase change of AP, was a large exotherm (2300 J/g) observed. When there was only 20 wt % sucrose, there was no exotherm visible in the DSC trace until after the AP phase change (the SDT trace differed). Likewise, the mix of AP with erythritol did not exotherm until the AP phase change, but heat release was observed from immediately after the phase change ( $\sim 247^\circ\text{C}$ ) to a maximum at around 438°C. In the thermograms of the AP/charcoal (mix 69) no exotherms were observed until after the AP phase change, at 247°C; however, where the first exotherms were observed depended on whether the sample was a sealed DSC sample or an open SDT sample. This observation was true for the AP sugars discussed above and the AP/sulfur (mix 85). For AP/charcoal a single sharp exotherm was observed around 456°C ( $\sim 900$  J/g) in the DSC trace but at 343°C ( $\sim 2000$  J/g) in the SDT trace (Fig. 12). This difference between the DSC and SDT traces was noted in other mixtures, but in those cases it was attributed to the volatilization of the fuel. However, with charcoal, fuel volatility was not a possible explanation. AP thermal decomposition is known to be particularly sensitive to pressure [9, 17].

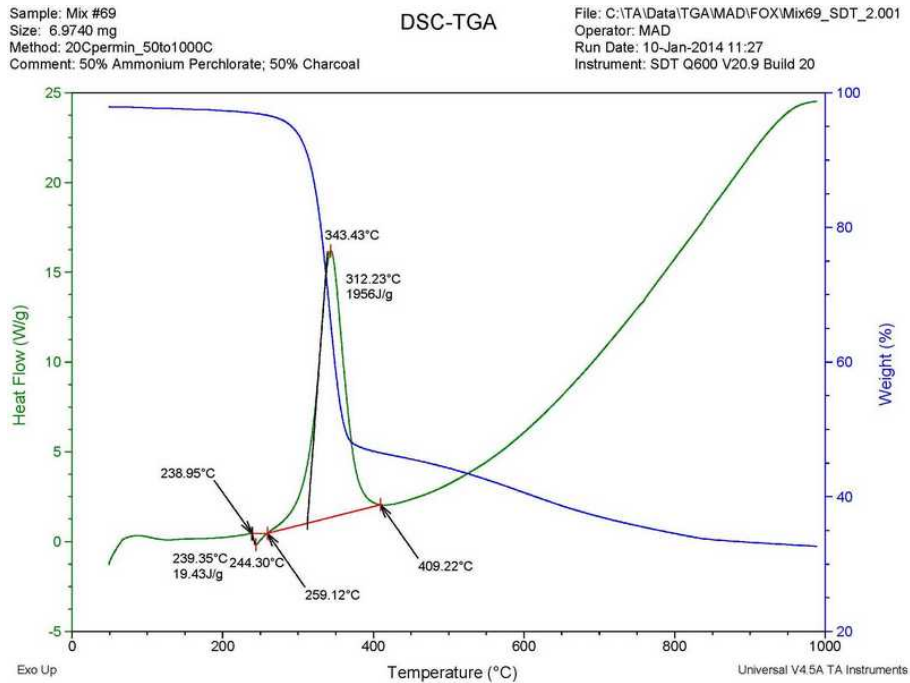
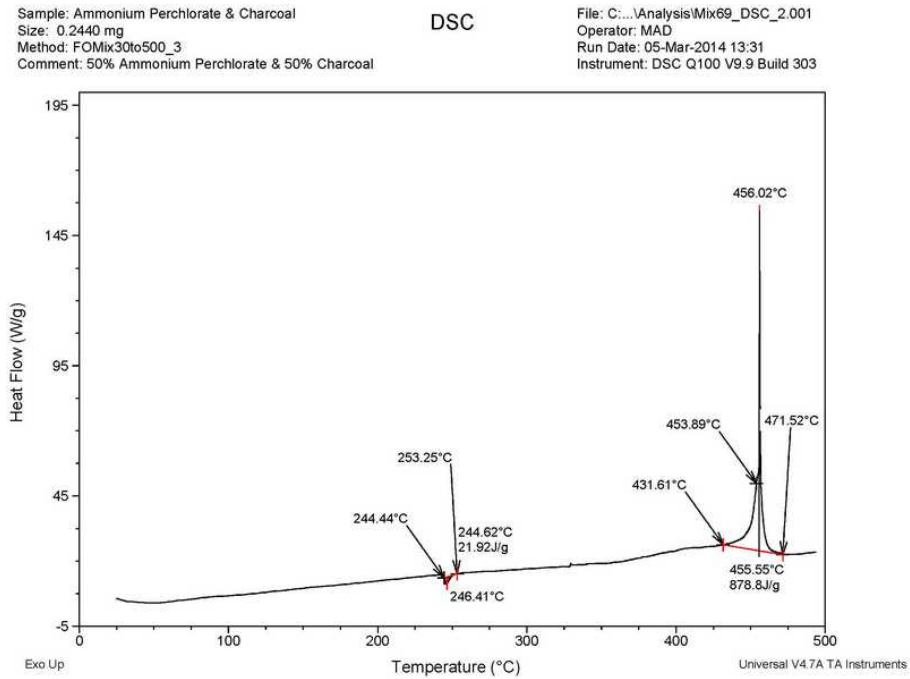
### 3.2.7 Nitrate

Although sucrose and  $\text{KNO}_3$  underwent several endothermic events (melt of sucrose, phase change of  $\text{KNO}_3$ ), the decomposition of sucrose/ $\text{KNO}_3$  mixtures did not begin until after the nitrate had melted (327°C). Thus, with the sugars, erythritols, and charcoal, decomposition was not observed until almost 400°C (Figs. 13 and 14). With sulfur as the fuel, decomposition was observed at almost 100° lower temperature. (It should be noted with 50/50 sucrose/nitrate a small exotherm indicative of sucrose decomposition was often seen at around 265°C.)

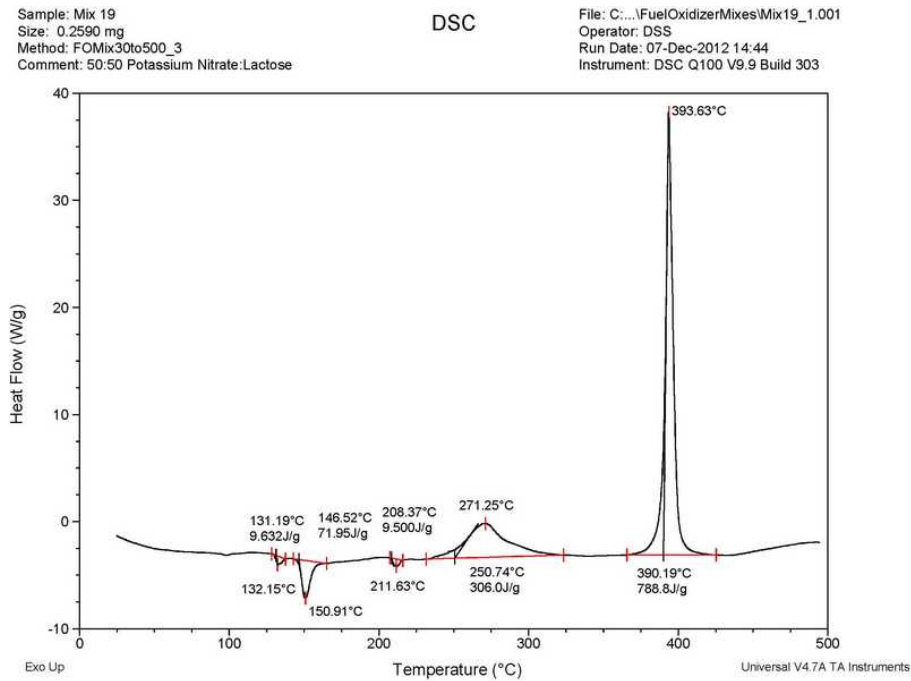
### 3.2.8 Nitrite

The DSC of  $\text{KNO}_2$  with 50 or 20 wt % sucrose showed one large exotherm (about 1500 J/g) immediately after the melt of the sucrose. Examination of the SDT shows the same exotherm centered around 250°C, but a majority of the heat was released (about 955 J/g) at higher temperature,  $\sim 446^\circ\text{C}$  (Fig. 15). Only with erythritol was the initial

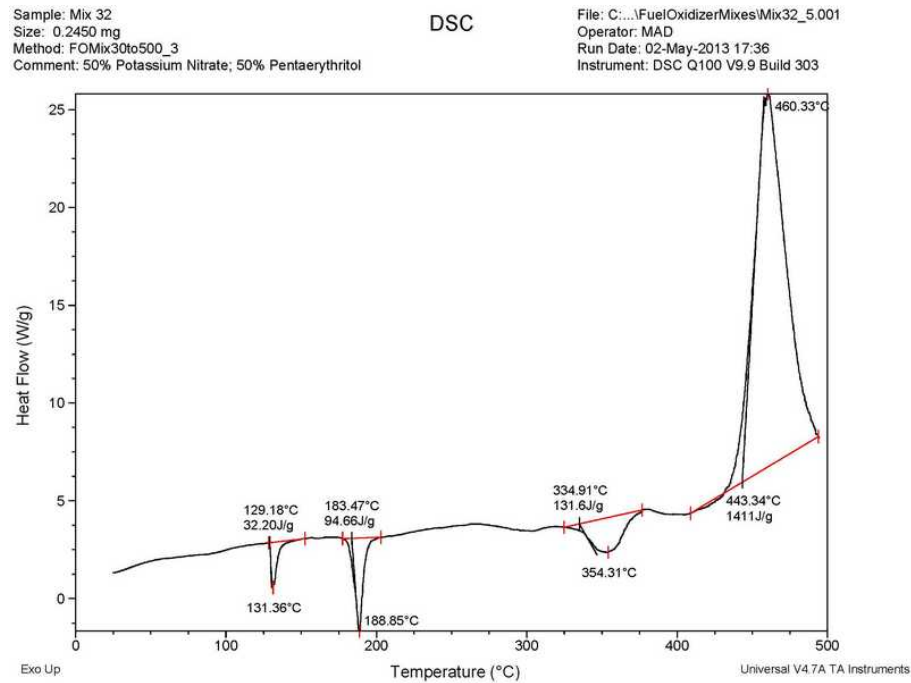




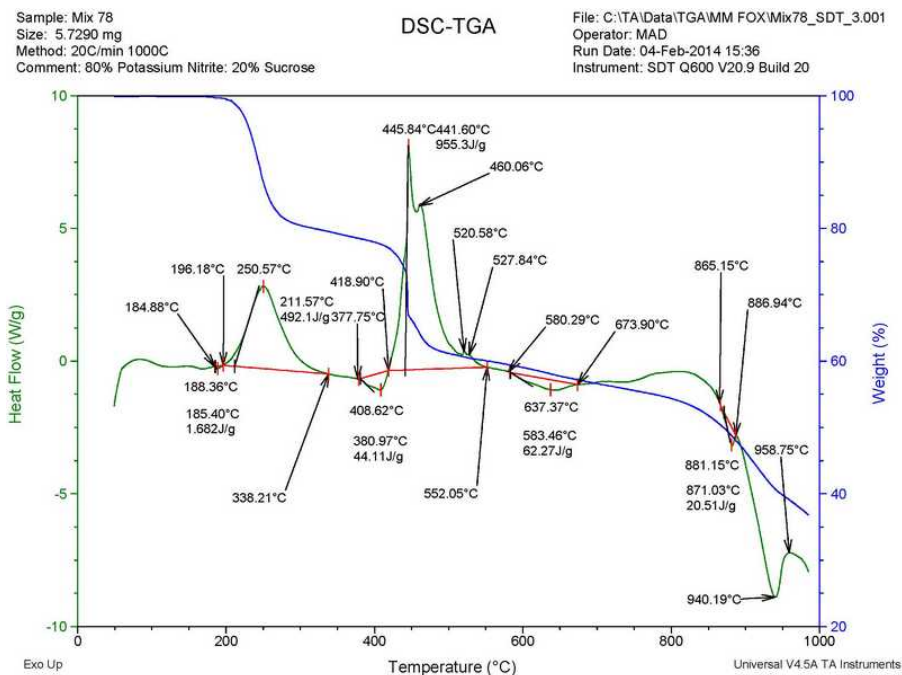
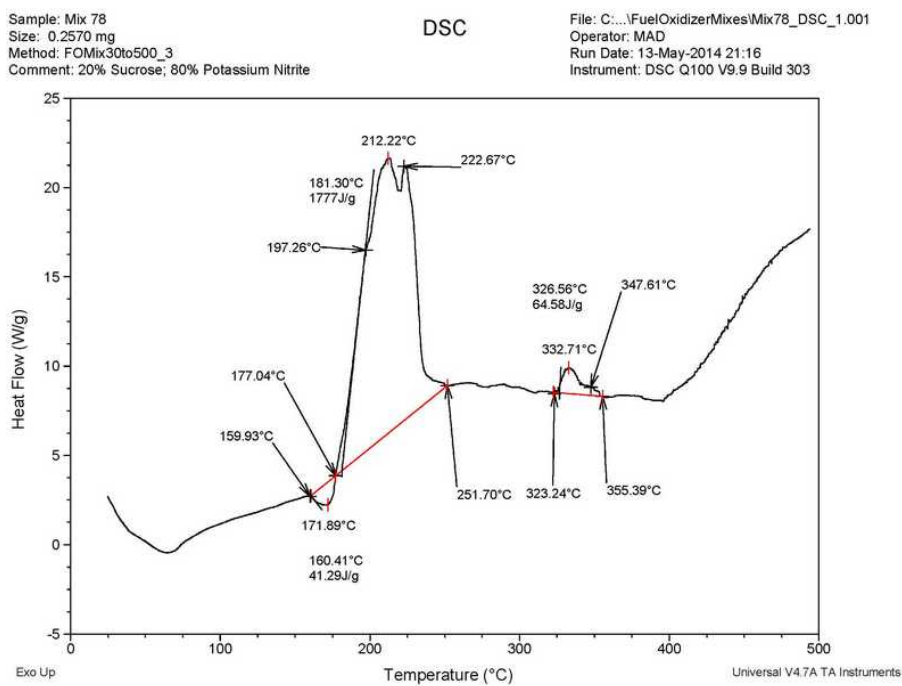
**FIG. 12:** AP +50% charcoal (mix 69)—DSC and SDT.



**FIG. 13:**  $\text{KNO}_3$  + 50% lactose (mix 19).



**FIG. 14:**  $\text{KNO}_3$  + 50% pentaerythritol (mix 32).

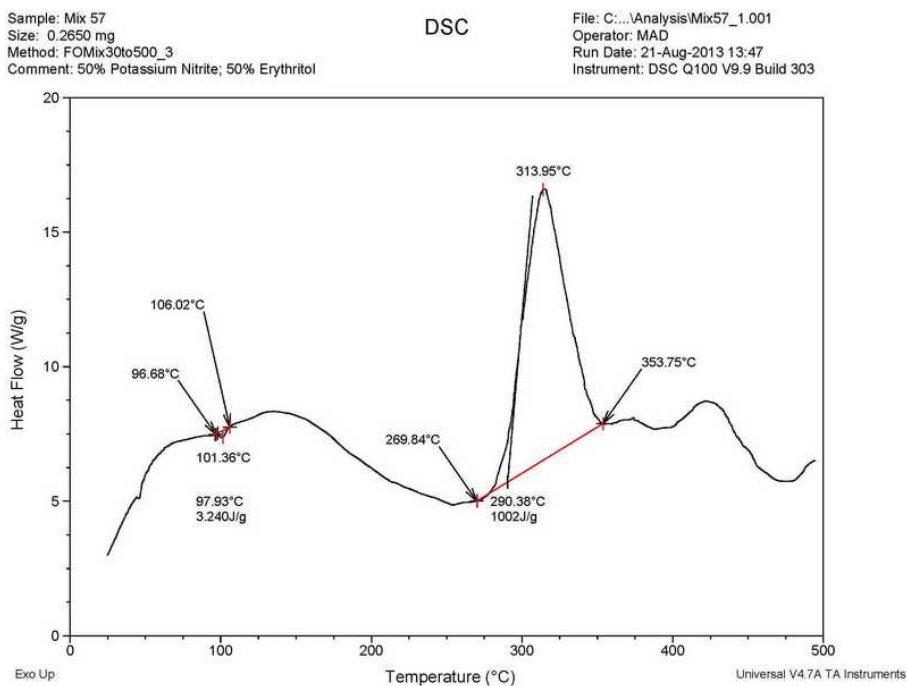


**FIG. 15:**  $\text{KNO}_2 + 20\%$  sucrose (mix 78)—DSC and SDT.

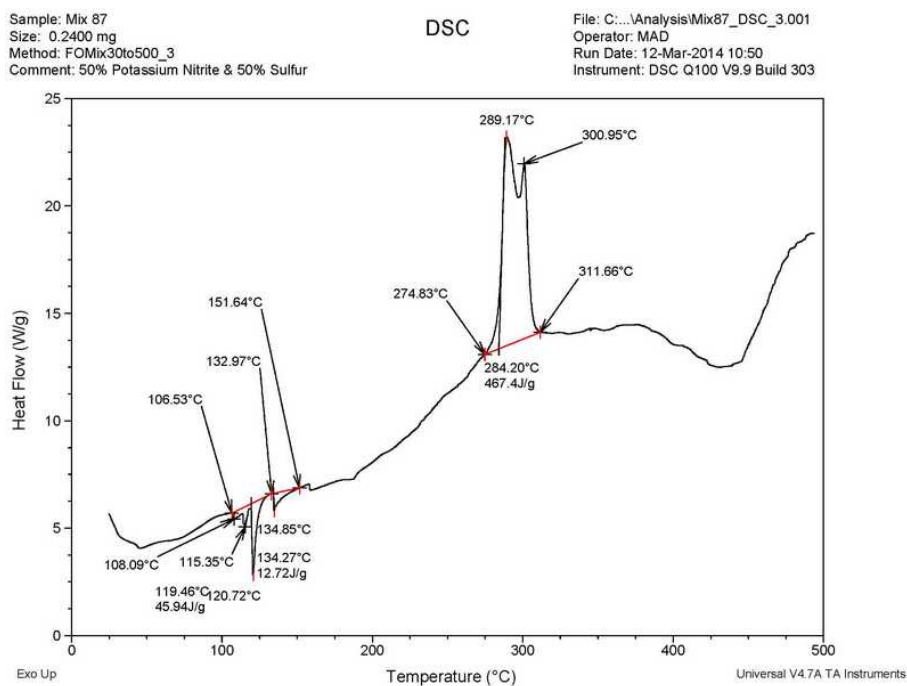
exotherm above 200°C. In mix 57,  $\text{KNO}_2$ /erythritol, the exotherm centered at around 318°C, around the temperature of the melt of  $\text{KNO}_2$  and the boiling point of erythritol (Fig. 16).  $\text{KNO}_2$  with 50 wt % sulfur showed a sharp exotherm maximum at around 290°C (Fig. 17).

### 3.2.9 Ammonium Nitrate

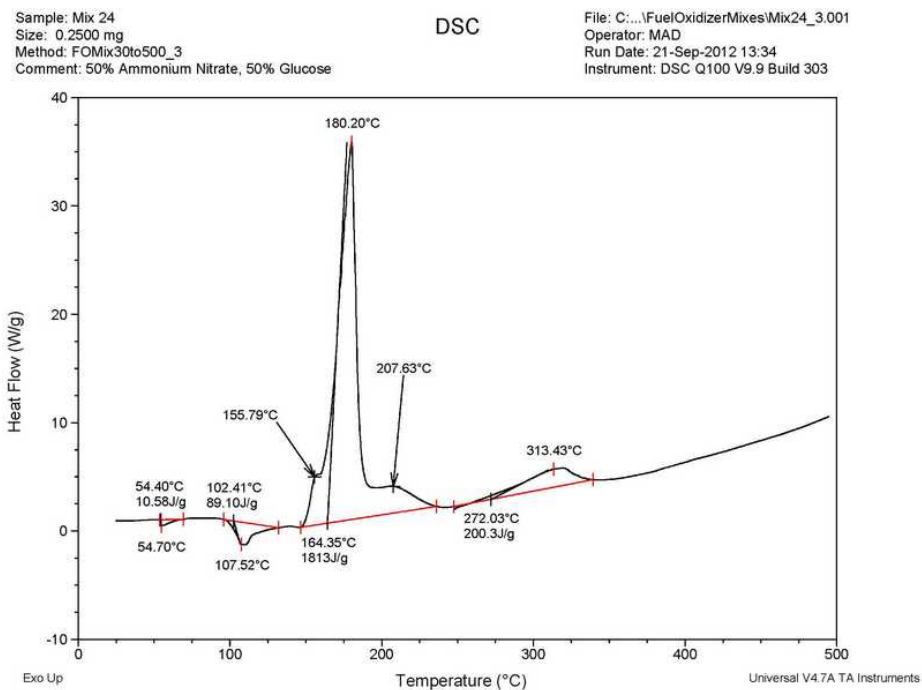
AN, like AP, released substantial energy ( $\sim 1500$  J/g) without added fuel. The exothermic maximum of AN with all sugars was around 170°C; this could be the melt of the sugars or that of  $\text{NH}_4\text{NO}_3$ . The fact that with fructose the reaction does not occur when the fructose is completely molten,  $\sim 120^\circ\text{C}$ , suggests the exothermic decomposition between AN and the sugars is facilitated when both species are molten (Figs. 18 and 19). In several of the thermograms with only 20% sucrose, heat release was not only observed at around 170°C, but also a significant, sometimes equal, exotherm at around 300°C. Despite various endotherms, the erythritols produced a single sharp exotherm at around 270°C, which is close to the normal decomposition temperature of AN. With sulfur (mix 39) and with charcoal (mix 41) the exothermic events occurred about 220°C, after the melting point of ammonium nitrate but earlier than its normal decomposition temperature (Figs. 20 and 21). The reaction with charcoal appeared at lower temperature than with any other oxidizer.



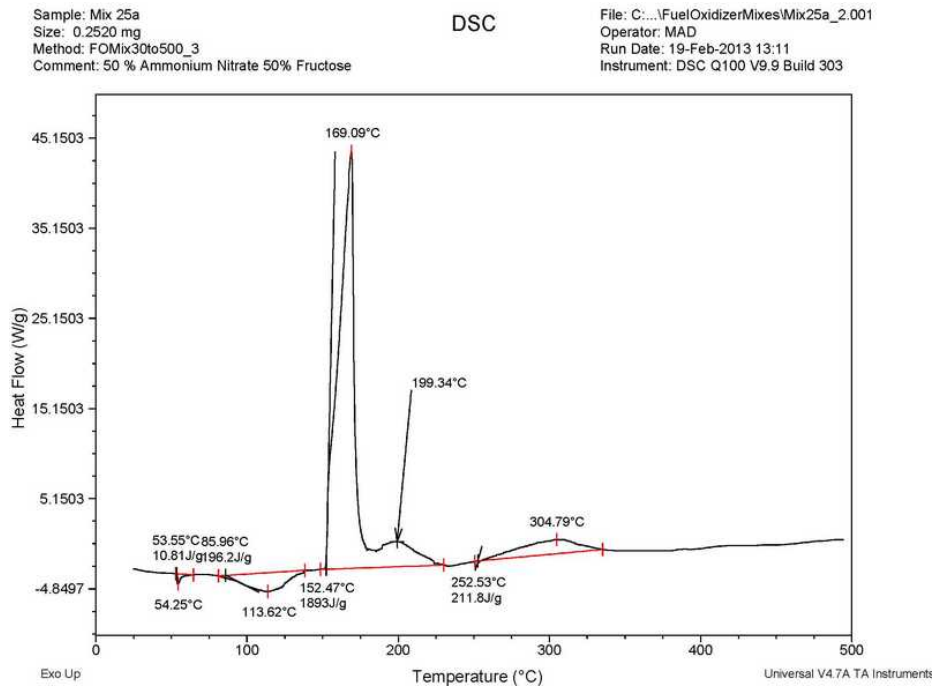
**FIG. 16:**  $\text{KNO}_2$  + 50% erythritol (mix 57).



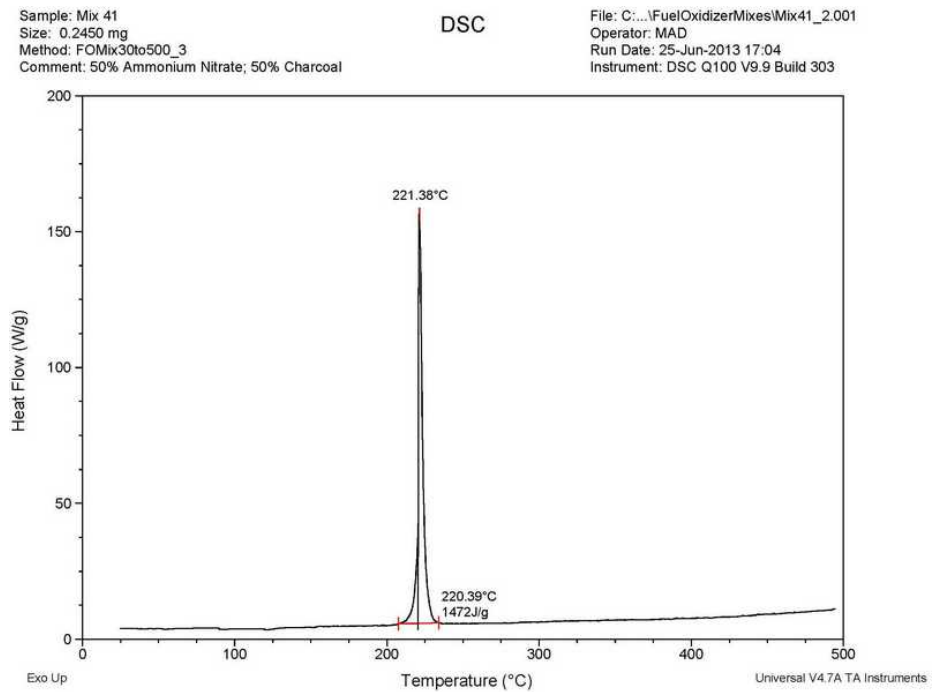
**FIG. 17:** KNO<sub>2</sub> + 50% sulfur (mix 87).



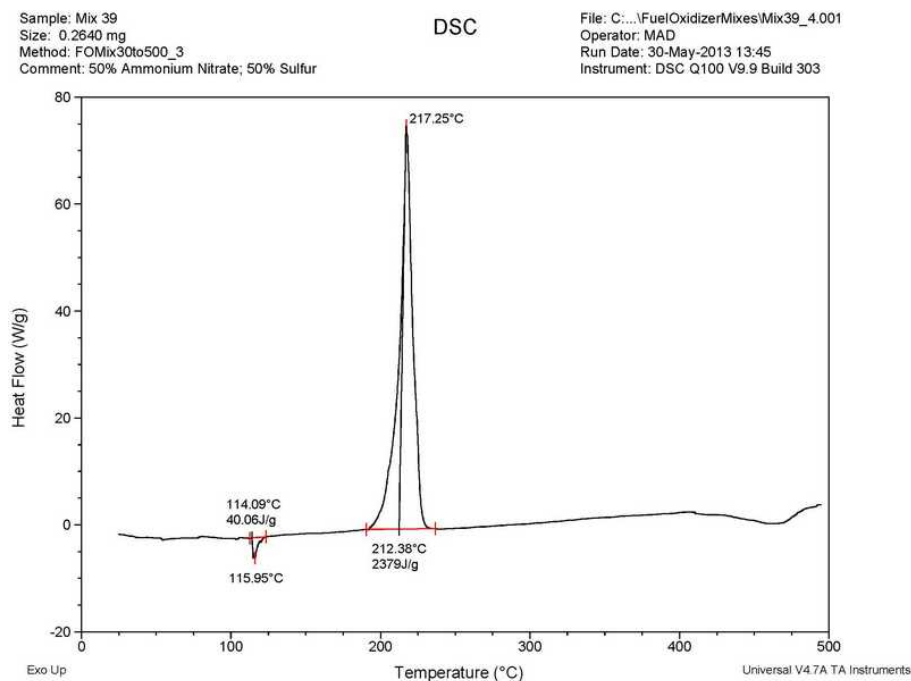
**FIG. 18:** AN + 50% glucose (mix 24).



**FIG. 19: AN + 50% fructose (mix 25a).**



**FIG. 20: AN + 50% charcoal (mix 41).**



**FIG. 21:** AN + 50% sulfur (mix 39).

### 3.2.10 Permanganate

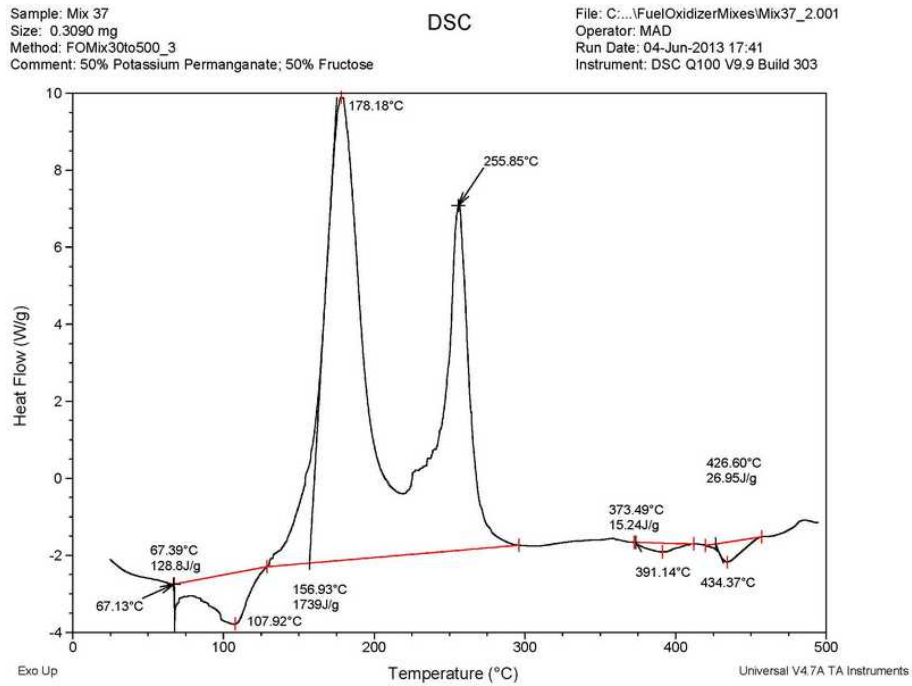
Permanganate itself has a complex decomposition pattern [18]. As with many of the other oxidizers, the exotherm of the sugar permanganate mix started as soon as the sugar melted (sucrose, fructose, or erythritol) [19]. The exothermic region lasts through the melt of  $\text{KMnO}_4$ . With fructose, decomposition also began as soon as the fructose melted, and the second exotherm occurred at the temperature where fructose decomposed  $\sim 260^\circ\text{C}$  (Fig. 22). The DSC of  $\text{KMnO}_4$  with sulfur reached a maximum at around  $309^\circ\text{C}$ – $331^\circ\text{C}$ , where permanganate alone would decompose (Fig. 23).

### 3.2.11 Dichromate

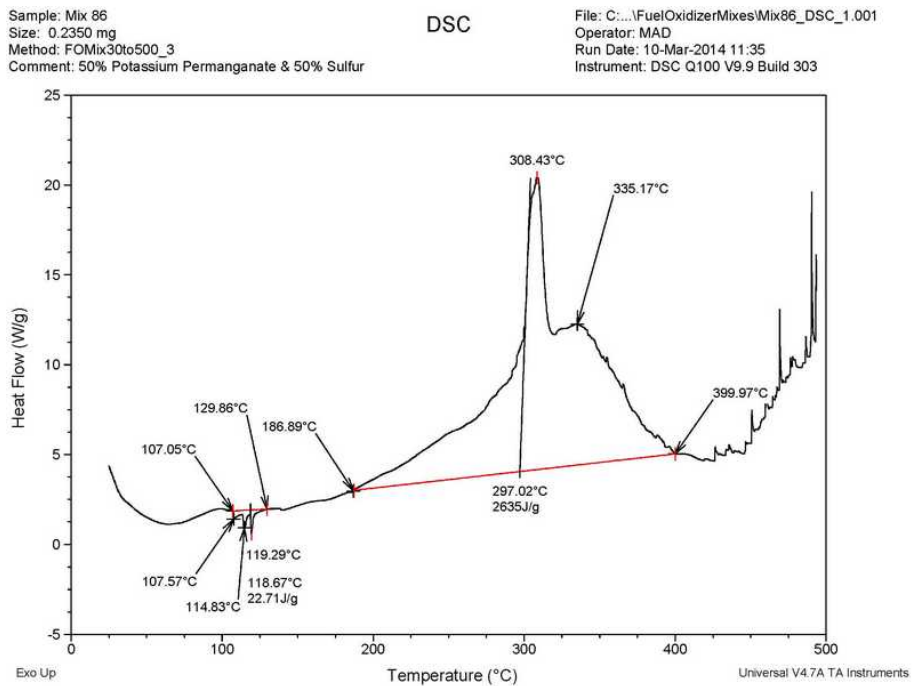
Little heat release was seen from the dichromate mixtures with sucrose, fructose, erythritol, or charcoal [20]. With the sugars the only exotherm observed was that correlated with the decomposition of the sugar itself, around  $240^\circ\text{C}$  (Fig. 24). With fructose or erythritol there was a small exotherm at  $\sim 398^\circ\text{C}$ , the melt of  $\text{K}_2\text{Cr}_2\text{O}_7$  (Fig. 25).

## 4. SUMMARY

Thermograms of the oxidizers alone were complex, including phase change(s), decomposition, and melts of the decomposition products. Use of the open pans in the SDT

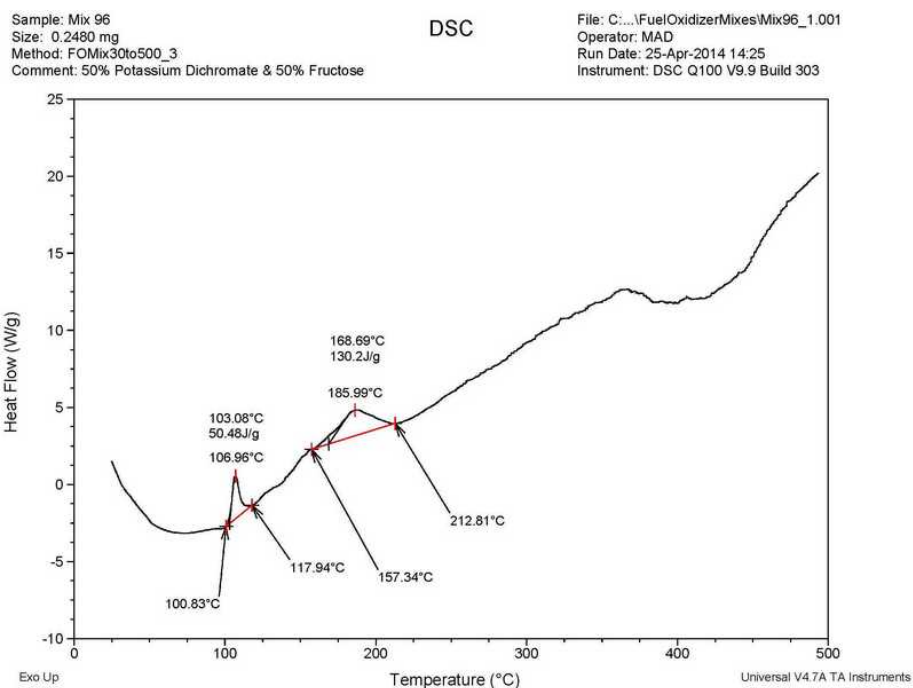


**FIG. 22:**  $\text{KMnO}_4$  + 50% fructose (mix 37).

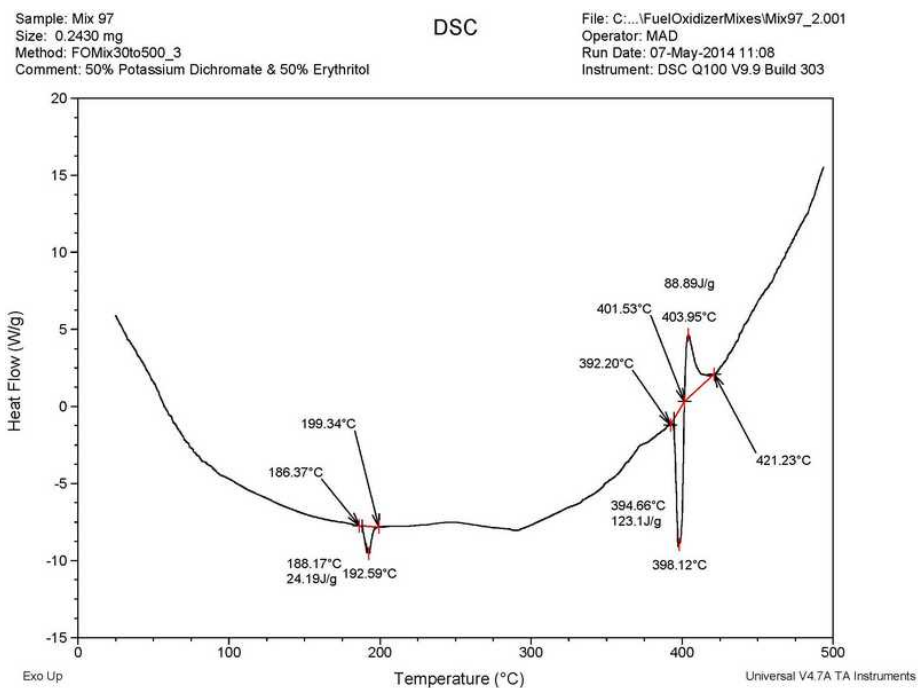


**FIG. 23:**  $\text{KMnO}_4$  + 50% sulfur (mix 86).





**FIG. 24:**  $K_2Cr_2O_7$  + 50% fructose (mix 96).

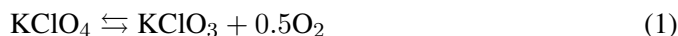


**FIG. 25:**  $K_2Cr_2O_7$  + 50% erythritol (mix 97).

further complicated thermal scans, with vaporization of some components competing with decomposition.

Interestingly, neat oxidizers appeared to undergo decomposition roughly in line with standard reduction potentials (Table 2) [21]. Most of the oxidizers produced some heat when decomposed without fuel, but it is a few hundreds of joules per gram compared to 1500 to 3000 J/g when decomposed with fuel. The exceptions, of course, are the ammonium salts, which produce 1000–1500 J/g without fuel and double that with fuel.

The oxides of chlorine released the most heat, which is in line with the general trend that the larger the electronegative difference between oxygen and the central element, the more stable the oxyhalide. This order of stability was attributed to the degree of pi-bonding in each species:  $\text{ClO}_4^- > \text{ClO}_3^-$  and  $\text{NO}_3^- > \text{NO}_2^-$  [22, 23]. Among the oxo-chlorine or oxo-nitrogen species, perchlorate and nitrate are more stable than the less highly oxidized chlorate and nitrite. Chlorates are generally more sensitive than perchlorates. If oxygen is not allowed to escape, the pairs nitrate/nitrite, perchlorate/chlorate, and periodate/iodate can establish a pseudoequilibrium, Eqs. (1)–(3) [22].



For the oxyhalides the final product, as temperature was ramped to above 700°C, was the potassium halide, and appropriate endotherms were observed in the SDT thermogram. Details of the chlorine oxides are complicated. In a combination of controlling reactions, simplified as Eqs. (1) and (2), perchlorate decomposes to form chlorate and chloride, melting, and further decomposing until decomposition produces a resolidification and complete decomposition occurs [4, 24]. For the nitrate/nitrite pair in an enclosed environment, this occurs in the temperature regime 550°C–750°C [24]:



$\text{KNO}_3$  undergoes an orthorhombic to rhombohedral transformation at  $\sim 130^\circ\text{C}$  and melts ( $333^\circ\text{C}$ – $334^\circ\text{C}$ ) to a liquid stable to  $550^\circ\text{C}$ . Above that the quasiequilibrium [Eq. (3)] sets in depending on the experimental conditions [25]. The decomposition of potassium nitrate and nitrite can produce  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{N}_2$ , and, finally,  $\text{K}_2\text{O}$ .  $\text{KNO}_2$  is reported to evolve  $\text{NO}_2$  at  $410^\circ\text{C}$ , which is below its melting point ( $440^\circ\text{C}$ ). This continues as the temperature is raised and  $\text{KNO}_3$  can be formed. Since the nitrate is more stable than the nitrite, it takes a higher temperature to result in complete decomposition [24].

In this study, DSC heat release values had standard deviation plural of over 25%. Some of the variation in heat release may have been poor mixing, despite the use of an acoustic mixer. However, in the past we have found that even scanning ammonium nitrate alone resulted in a 15% variation. We suspect that with energetic materials it may be difficult for the thermocouples to accurately track the fast release of heat. Nevertheless, the poorest oxidizer in terms of heat release was clearly potassium dichromate, with

roughly 100–200 J/g heat release with the chosen fuels. The rest of the oxidizers released heat ranging from 1100 to 2200 J/g with an average of 1500 J/g, regardless of the fuel. Of those oxidizers, nitrite released the least heat  $\sim 1000$  J/g, while the two ammonium salts and chlorate release the most heat.

Experimentally it was found that differences in DSC and SDT traces appeared to be related to the ability of reactants/products to vaporize in the SDT open containers. Evidence for this interpretation was threefold. First, occasionally exotherms in the DSC where containers were sealed appeared as endotherms in SDT where they were not sealed. Second, certain prominent well-behaved exotherms by DSC were sometimes split into two exotherms by an overlapping endotherm. Third, total heat released was usually lower in the open crucibles compared to the closed capillary tubes.

When fuels were added to the oxidizer, the thermograms became more complicated. Lack of mixture homogeneity played a role, as did heating rate. It has been shown that ignition temperatures are affected by sample weight and heating rates [26]. Particle size has been mentioned as important. We and others [27, 28] have shown that particle size can affect the temperature at which the exotherm is observed (Fig. 26). Large particles are harder to mix homogeneously throughout the mixture; they are harder to ignite on purpose, and it is easier to accidentally “excite” them. These issues make smaller particles preferable, but handling them can be a major problem.

With the exception of charcoal, all the fuels chosen for this study melted below 200°C. With the sugars, the first exotherms often occurred after the melt. In DSC scans this often appears as one large, broad exotherm having an energy content of 1000–2000 J/g. To ensure this observation was not a result of excess fuel, each oxidizer was heated

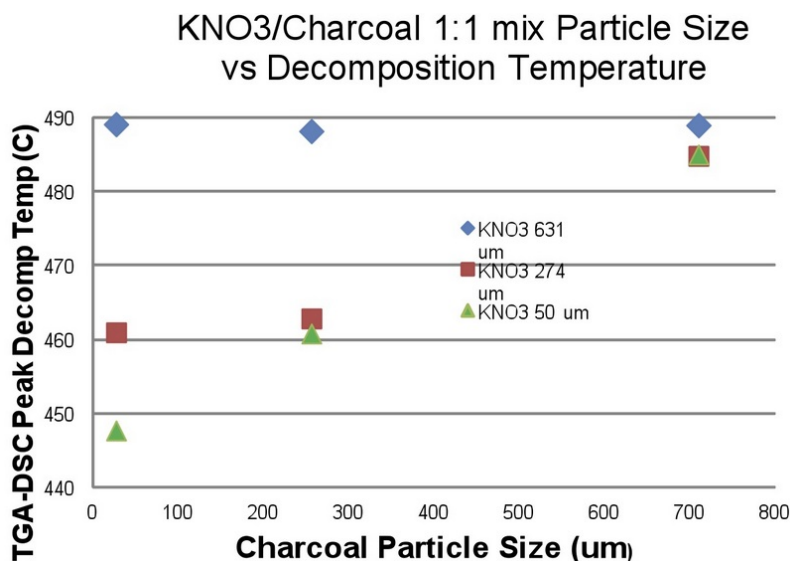


FIG. 26: Effect of particle size on DSC exothermic temperature.

with 20 wt % sucrose (i.e., below stoichiometric proportions). Three different behaviors were observed and are cataloged in Table 4.

In mixtures where DSC traces indicate appearances of exotherms during the fuel melt, SDT also demonstrated exotherms at similar positions but one or more exotherms appeared later in the scan. There was often an exotherm at around 300–350°C, where  $\text{KIO}_4$  and  $\text{KMnO}_4$  decompose and  $\text{KNO}_3$ ,  $\text{KNO}_2$ ,  $\text{KClO}_3$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$  experience phase changes or melts. For  $\text{KIO}_4$  the 350°C exotherm signals its decomposition. For the neat oxidizer this decomposition was conversion into  $\text{KIO}_3$ ; the rest of the thermal scan (up to 1000°C) was identical to that observed for  $\text{KIO}_3$ . Decomposition of the 50/50 chlorate/lactose mixture has been examined in detail [14]. As in this study, perchlorate formation was not observed. Interconversion of oxidizers becomes unimportant compared to the reaction with the fuel [Eq. (4)]. It is speculated that the decomposition of the chlorate was initiated when molten lactose partially solubilizes  $\text{KClO}_3$ . Solvents with OH groups readily dissolved chlorate. We now extend that observation to a number of oxidizers.



With the exception of charcoal all fuels used in the study melted below 200°C. It was found that decomposition of the mixture was usually initiated by a thermal “event” in the oxidizer or the fuel. This behavior was so general that we have classified the decomposition of the fuel-oxidizer mixtures as fuel or oxidizer controlled. Oxidizer-controlled mixtures, such as those made with  $\text{KClO}_4$ ,  $\text{NH}_4\text{ClO}_4$ , or  $\text{KNO}_3$ , did not exhibit substantial exotherms until the oxidizer underwent a phase change or decomposition (Table 5). Fuel-controlled mixtures underwent decomposition immediately after the fuel melt; this was the case when  $\text{KIO}_4$ ,  $\text{KIO}_3$ ,  $\text{KBrO}_3$ ,  $\text{KNO}_2$ ,  $\text{KMnO}_4$ , and  $\text{KClO}_3$  were mixed with the sugars. Fuel-controlled mixtures exhibited lower decomposition temperatures than oxidizer-controlled mixtures. With AN/sugar mixtures the melting point of the sugars and that of the AN were very close,  $\sim 170^\circ\text{C}$ ; thus it was difficult to assign these mixtures as oxidizer or fuel controlled. However, when AN was mixed with pentaerythritol or erythritol, the exothermic maximum was essentially the same in both cases,  $\sim 270^\circ\text{C}$ , which is above the melt of the erythritols and AN, but near the normal decomposition temperature of AN.

**TABLE 4:** Oxidizers with 20 wt % sucrose (DSC response and average J/g)

First exotherm after fuel melt	$\text{KIO}_4$	*	$\text{KIO}_3$	*	$\text{KBrO}_3$	*	$\text{KNO}_2$	*
	1603	2	838	5	2239	4	1689	2
Principle exotherm follows melt but also other exotherms	$\text{KClO}_3$		$\text{KMnO}_4$		$\text{NH}_4\text{NO}_3$			
	2413	4	1798	2	2809	3		
First exotherm oxidizer controlled	$\text{KNO}_3$		$\text{NH}_4\text{ClO}_4$		$\text{KClO}_4$		$\text{KCr}_2\text{O}_7$	
	967	2	1357	3	800+		102	

\* Number of scans averaged

**TABLE 5:** Oxidizers with 50wt% fuel DSC response & average J/g (number runs)

	KIO <sub>4</sub>	KIO <sub>3</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	KClO <sub>4</sub>	NH <sub>4</sub> ClO <sub>4</sub>	KNO <sub>3</sub>	KNO <sub>2</sub>	NH <sub>4</sub> NO <sub>3</sub>	KMnO <sub>4</sub>	KCr <sub>2</sub> O <sub>7</sub>
Thermal change	350 °C	553 °C	417, 460 °C	350, 415 °C	305 °C	248, 400 °C	133, 330 °C	323, 430 °C	130, 167, 316 °C	260, 305 °C	398
Sugars (130–190°C)	melt	melt	melt	melt+	>400	melt+ >248	262, >330	melt	melt AN & fuel	melt+	>398
Peak temperature °C	167	187	206	175	495 sdt	338	386	254	171	239	402
J/g for 50 wt% sucrose	2054	1643	1110	2033	1320	2341	926	1231	2136	1169	50
PE (190, 233, 305)	–	–	–	melt+	–	–	>400	–	269+	–	–
Peak temperature °C	–	–	–	270	–	–	471	–	267	–	–
Heat released J/g	–	–	–	1797	–	–	1669	–	2087	–	–
Erythritol (124, 330)	melt+	melt	melt+	200	>305+	>248+ >400	>400	270	270	melt+	>398
Peak temperature °C	142	185	229	253	181	313	413	316	5 269	325	390
Heat released J/g	1327	871	1160	2314	881	3616	2471	1014	5 1817	1836	129
Sulfur (116, 180, 315)	250	220	–	150	>400	>248	~300	290	170	270	–
Peak temperature °C	303	298	–	194	468	422	333	299	219	309	–
Heat released J/g	1410	659	–	1031	1612	1747	916	1006	3 2103	808	3
Charcoal	–	–	–	335	>400	>248	>400	–	223	–	>398
Peak temperature °C	–	–	–	–	526 sdt	450	467	–	–	–	–
Heat released J/g	–	–	–	1470	1482	951	1403	–	1611	–	100
			fuel controlling		oxidizer controlling						fuel or oxidizer controlled

PE and erythritol (ET), both polyalcohols, were included in this study for comparison with the sugars. Since with a number of oxidizer mixtures the melt of the fuel initiated decomposition, it was thought that an alcohol with a higher melting point would impart greater thermal stability. PE (m.p. 191°C) and ET (115°C) were chosen to bracket the melting points of the sugars used in this study. It was expected that PE would impart slightly greater thermal stability to the fuel-oxidizer mixtures. For the three oxidizers (KClO<sub>3</sub>, KNO<sub>3</sub>, AN) which were examined with both erythritol and pentaerythritol, the decomposition temperature with PE was raised only slightly or not at all. The chlorate/PE mix had an exotherm which initiated immediately after the PE melt (191°C), peak maximum ~270°C. The chlorate/ET mixture had an exotherm around 253°C, but this is 50 to 60° above its melt. KNO<sub>3</sub> mixtures with any of the fuels did not experience exotherm until near its melt at 330°C; for PE and ET this resulted in peak maxima around 470°C and 413°C, respectively.

An illustration of one component control was observed in the four oxidizer mixtures containing charcoal. In three cases, the melt of the oxidizer controlled the temperature at which the exotherm of the mixture appeared: KClO<sub>3</sub> 336°C (m.p.), KClO<sub>4</sub> 520°C (m.p.), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 400°C (m.p.). In the fourth case, the oxidizer, AP, did not melt, and the exothermic reaction between it and charcoal occurred above the highest AP exotherm.

Sulfur is a low-melting inorganic fuel often used as part of pyrotechnic formulations. It is this low-melting property which is generally believed to make the addition of sulfur to pyrotechnic mixtures hazardous. However, only with chlorate and AN did the combination with sulfur result in exotherms around 200°C or lower. With periodate and iodate the exotherm occurs around 220°C to 250°C, which could have been connected to the polymerization of sulfur.

While heat release values had standard deviations on the order of 25%, the poorest oxidizer was clearly potassium dichromate, which yielded barely 100 J/g. The rest of the oxidizers released heat ranging from 1100 to 2200 J/g, with an average of about 1500 J/g, regardless of the fuel employed. Of those oxidizers, nitrite was the poorest, and the best were ammonium perchlorate, ammonium nitrate, and potassium chlorate. No fuel stood out as clearly the "best" in terms of releasing the most heat; they averaged 1500 J/g by DSC analysis. Response to hot-wire ignition was assessed by the length of the burn and the light output. Table 2 orders the oxidizers left to right as highest oxidizing power to lowest in terms of electromotive potential. This trend is roughly followed by burn time, either measured visually or by light-sensitive detector. The fastest burn time oxidizers are on the left (highest oxidizing power) and those with longest burn times are on the right. Light output, when the fuel was sucrose, did not show a clear trend. However, when the fuel was aluminum, those on the furthest to the right of the table, i.e., those with the lowest oxidation potential, failed to light the aluminum. Seemingly out of place in this series is AN, which is high in heat output, and dichromate, which is extremely low in heat output.

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