Green Liquid Oxidizers Basing on Solutions of ADN and AN in Hydrogen Peroxide for Hypergolic Propellants with High Performance

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Abstract

Hydrazine replacement in hypergolic rocket and satellite propulsion requires new green energetic oxidizers. In this paper, an approach is investigated basing on concentrated hydrogen peroxide with purities from 60% to 94%. In scope to reduce the melting or glass transition temperature and to increase stability but also to increase the oxygen balance and performance, ammonium nitrate (AN), ammonium dinitramide (ADN) and urea hydrogen peroxide (Carbamide) were solved in hydrogen peroxide. Such oxidizers enable low operation temperatures far below -40 °C. 40 oxidizers were produced and tested as hypergolic propellants in combination with an energetic ionic liquid (EIL) basing on AMIM DCA as fuel including appropriate catalysts enforcing hydrogen peroxide decomposition. Such systems provide a theoretical specific impulse up to >2600 N s/kg or 3750 N s/dm^3 and should suite as liquid or gelled propellants. Hypergolic lab scale ignition tests result in ignition delay times comparable to hypergolic systems in operation. The results were discussed in comparison to thermodynamic reaction data of the oxidizer and the bi-propellant with measured temperatures. Especially, it was found that the ignition delay time correlates with the inverse of the oxygen balance and the decomposition temperature of the oxidizer and also with the adiabatic combustion temperature of oxidizer fuel combination.

1. Introduction

Hypergolic systems are preferable for easy and reliable ignition and the possibility of repeatable turning thrust off and on. On this reason, hypergolic bi-propellants have been investigated and developed since the first half of the twentieth century. The first hypergolic system in service was hydrogen peroxide with a mixture of hydrazine hydrate, methanol and potassium tetracyanocuprate as a catalyst applied in the German rocket-powered fighter aircraft Me 163 [1]. Actually, hypergolic systems in use still consist of hydrazine and its derivatives, such as unsymmetrical dimethylhydrazine (UDMH) and monomethylhydrazine (MMH) in combination with red fuming nitric acid (RFNA, HNO$_3$) or dinitrogen tetroxide (NTO, N$_2$O$_4$) [2][3]. The disadvantage of these systems is the toxic nature of hydrazine and its derivatives and the aggressiveness of RFNA and N$_2$O$_4$ that do not fulfil the requirements for current environmental demands and easy handling [4]. High-concentrated hydrogen peroxide (HTP, H$_2$O$_2$) [5] maybe an alternative but suffer in long-term stability and freeze out at low temperatures [6][7].

One way out may be solutions of oxidizer salts such as ammonium nitrate (AN) or ammonium dinitramide (ADN), which show low melting or glass transition points without ruining the oxygen balance of the oxidizer [8]. Basing on these results, further solutions in commercially available, concentrated hydrogen peroxide (HTP) with a purity of 60% to 80% were investigated. In scope to increase stability and hydrogen peroxide concentration also urea hydrogen peroxide (Carbamide Peroxide) was added.

In contrast to hypergolic oxidizers in use no hazardous or aggressive components are included and the systems offer low operation temperatures.

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2. Propellants

2.1 Oxidizer Compositions

Hydrogen peroxide was purchased from Evonic Industries in 60% and 70% solutions. Nearly pure hydrogen peroxide (99.8%) was produced using a fractional freezing process of HTP (High Test Peroxide) purchased from DEGUSSA [10].
ADN and AN decrease the melting point of hydrogen peroxide solutions with a simultaneous increase of the density. ADN was purchased from Bofors, Sweden.
As stabilizer, urea was tested and added to some of the compositions. Urea was introduced as hydrogen peroxide - urea crystals with the intent to increase simultaneously the hydrogen-peroxide content.
40 oxidizer solutions were produced and investigated including:

Hydrogen peroxide:	60, 70, 80, 90, 94% (purity)
Ammonium nitrate (AN):	0 – 20%
Ammonium dinitramide (ADN):	0 – 40%
Urea hydrogen peroxide:	0 – 4%

In Table 1 the mass compositions of all oxidizer mixtures are summarized. Additionally, the resulting purity of the used hydrogen peroxide is mentioned in brackets behind the mass percent of total hydrogen peroxide. Hydrogen peroxide with 70% purity and high-concentrated hydrogen peroxide received by fractional freezing with a purity of about 95% were used as reference.
The third last and second last columns contain the oxygen balance (OB) and the adiabatic temperature of the pure oxidizer decomposition calculated with the ICT-Thermodynamic Code [11]. The latter one is an indication of energetic performance and is interesting for discussing the ignition delay time and varies from approx. 400 K to 1460 K mainly influenced by the purity of hydrogen peroxide. But also the partial replacement of AN by ADN increases the adiabatic temperature of the oxidizer.
The last column lists the melting or glass transition points measured via DSC. All oxidizers labeled with an asterisk (*) showed only a glass transition temperature at -120 °C and no other melting points were observed in repeated and cycled measurements. Also in DMA experiments (rotation mode) no abrupt rise of viscosity occurred. Actually it cannot be ruled out that these oxidizers are undercooled liquids and the crystallization starts after a longer period of time. So the results are promising for low operation temperatures but not definitely confirmed.
Figure 1a and b illustrate the variation of these parameters as function of hydrogen peroxide purity.
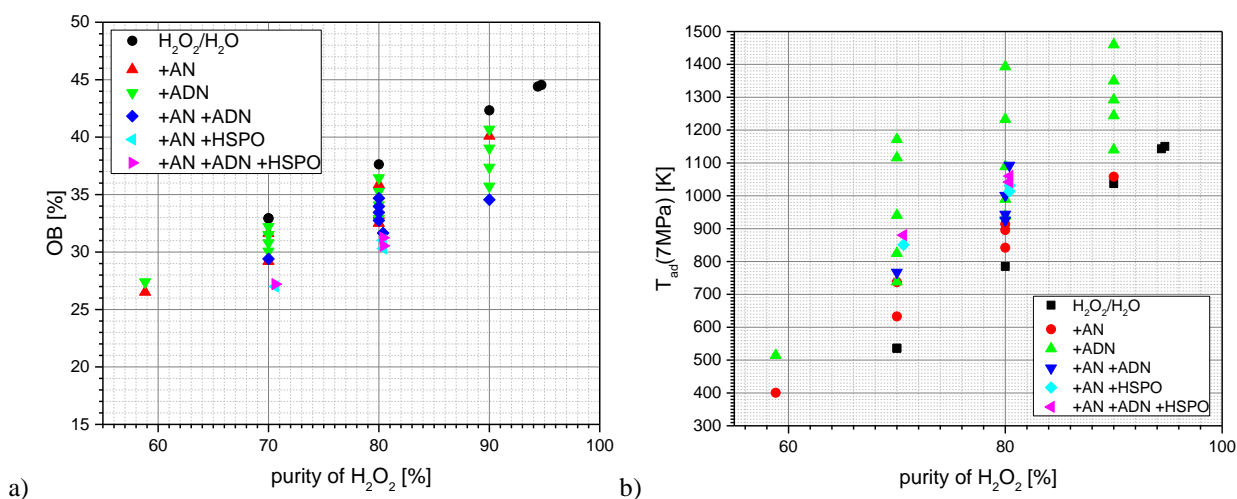

Figure 1 a) Oxygen balance (OB) and b) adiabatic temperature T_{ad} of oxidizer composition as function of the hydrogen peroxide purity segmented for solutes.

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Table 1 Oxidizer compositions including oxygen balance OB, adiabatic temperature T_{ad} (calculated for 1 bar with ICT-Thermodynamic Code) and measured melting point T_m or glass transition temperature T_g.

Oxidizer	H_2O_2 % (x% purity)	H_2O %	AN %	ADN %	Urea %	OB %	Tad K	T_m, T_g °C
H_2O_2 94.7%	94.7 (95%)	5.3	0	0	0	44.5	1145	-5
H_2O_2 90%	90 (90%)	10	0	0	0	42.3	1037	-11
H_2O_2 80%	80 (80%)	20	0	0	0	37.6	785	-25
H_2O_2 70%	70 (70%)	30	0	0	0	32.9	536	-38
JH Ox. 3	50 (60%)	35	15	0	0	26.5	401	-63
14/124	56 (70%)	24	0	20	0	31.5	825	-65.7
14/125	50 (60%)	35	0	15	0	27.4	515	-56.6
Ox AN 1	49.7 (70%)	21.3	29	0	0	29.2	737	-60.3
Ox AN 2	49.7 (70%)	21.3	25	4	0	29.4	767	-62.7
Ox AN 3	51.2 (70%)	21.3	25	0	2.6	27	851	-61.5
Ox AN 4	51.2 (70%)	21.3	21	4	2.6	27.2	880	-62.7
Ox AN 5	60 (80%)	15	25	0	0	33.2	896	*
Ox AN 6	60 (80%)	15	21	4	0	33.5	926	*
Ox AN 7	61.5 (80%)	15	21	0	2.6	31.0	1006	*
Ox AN 8	61.5 (80%)	15	17	4	2.6	31.3	1035	*
Ox AN 9	56.8 (80%)	14.2	29	0	0	32.5	914	*
Ox AN 10	56.8 (80%)	14.2	25	4	0	32.8	944	*
Ox AN 11	58.3 (80%)	14.2	25	0	2.6	30.3	1024	*
Ox AN 12	58.3 (80%)	14.2	21	4	2.6	30.5	1053	*
Ox AN 15	60 (80%)	15	12	13	0	34.0	993	*
Ox AN 16	61.5 (80%)	15	10	11	2.6	31.7	1087	*
VW04	81 (90%)	9	0	10	0	40.68	1140	
VW05	72 (90%)	8	0	20	0	39.03	1244	
VW06	63 (90%)	7	0	30	0	37.37	1350	
VW07	54 (90%)	6	0	40	0	35.72	1460	
VW08	72 (80%)	18	0	10	0	36.45	939	
VW09	64 (80%)	16	0	20	0	35.26	1089	
VW10	56 (80%)	14	0	30	0	34.08	1233	
VW11	48 (80%)	12	0	40	0	32.9	1393	
VW12	63 (70%)	27	0	10	0	32.21	738	
VW13	58 (70%)	24	0	20	0	31.5	941	
VW14	49 (70%)	21	0	30	0	30.79	1116	
VW15	42 (70%)	18	0	40	0	30.07	1172	
VW16	81 (90%)	9	10	0	0	40.1	1058	
VW17	72 (80%)	18	10	0	0	35.87	842	
VW18	63 (70%)	27	10	0	0	31.63	633	
VW19	54 (90%)	6	20	20	0	34.56	1292	
VW20	64 (80%)	16	10	10	0	34.68	990	

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2.2 Fuel

1-allyl-3-methylimidazolium dicyanamide (AMIM DCA) was used as fuel because of the results of a previous study about the hypergolic reaction with nitric acid [9]. AMIM DCA was purchased from IOLITEC and dried under HV and P_2O_5 for one week prior to use and gelled with MWCNTs. As an ionic liquid, AMIM DCA unlike conventional molecular liquids has practically no vapor phase. Therefore, significantly reduced environmental risk, better storage and handling properties are expected. AMIM DCA shows a broad operational temperature range (glass transition temperature -94 °C; purity: ≥98.5% (HPLC)). It is not sensitive to mechanical stimuli according to NATO STANAG 4487 and NATO STANAG 4489 procedures. For the hypergolic decomposition of hydrogen peroxide, a copper based catalyst was added to the fuel in an amount of 15%. This fuel is named as AMIM DCA(i).

Figure 2 plots the specific impulse of the oxidizer/fuel systems as function of the AMIM DCA(i) amount calculated with ICT-Thermodynamic Code [11] using an expansion ratio 70:1. The maxima results with an AMIM DCA amount of approx. 15 to 20%. When ADN is used as solute the maximum specific impulse exceeds a mass specific impulse of 2600 Ns/kg, which is the reference landmark for using pure hydrogen peroxide.
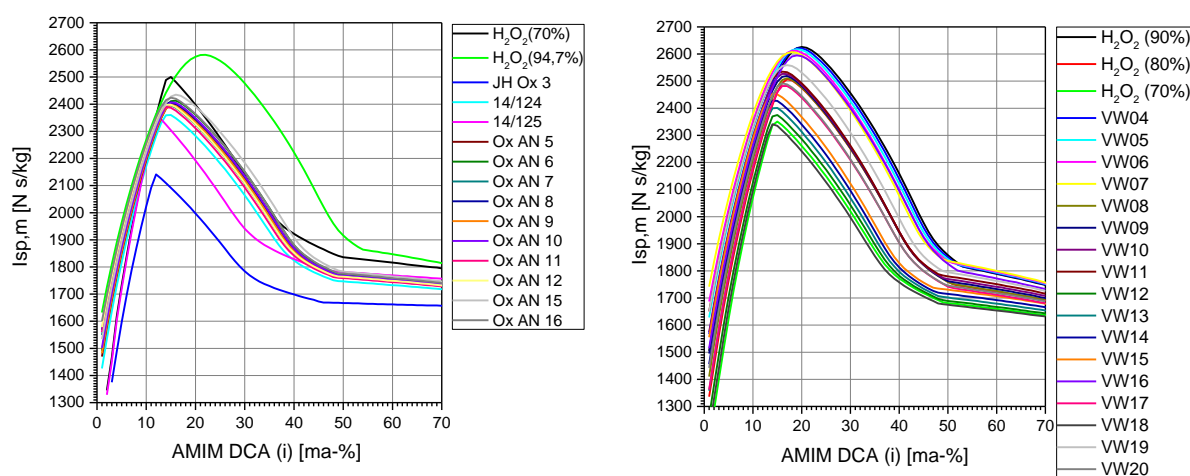

Figure 2 Mass impulse of the various oxidizer solutions in combination with AMIM DCA(i) (7 MPa : 0.1 MPa) (calculated with ICT-Thermodynamic Code).

3. Experimental set-up

The hypergolic behavior was tested in laboratory scale using a total fuel mass of 3 to 5 g. A defined amount of the oxidizer solution was injected into a polyethylene coquille containing the equivalent optimum mass of AMIM DCA fuel. Figure 3 illustrates the used set-up. The oxidizer and fuel mass were calculated according to the maximum specific impulse. But during the tests, the reaction often starts before the total oxidizer mass was completely injected. The reaction was observed using a Redlake Motion Pro X 24-bit color high-speed camera with a frame rate of 2000 fps. To measure the ignition delay time, each single picture was analyzed using the ICT-video-analyzer tool which is developed to investigate combustion movies with defined frame rate to determine ignition delay times and burning rates (Figure 4). Figure 5 shows some characteristic moments of the ignition and combustion sequence. As ignition delay time the period from the moment when the first drop of oxidizer impinges the fuel surface (0 ms) till the first appearance of an illuminating flame (31 ms) was determined. In between the oxidizer/fuel mixture starts intensively boiling producing large bubbles (27 ms). As ignition delay time, the shortest measured value of several tests was used (most best of three).

For non-intrusive determination of flame temperatures during the combustion process, a fast scanning MMS-spectrometer (ZEISS MCS 611 PGS-NIR 2.2) with a wavelength ranging from 950 nm to 2.15 μm was applied to record emission spectra with scan rates up to 60 spectra per second. Temperatures were achieved from the recorded spectra by using ICT-BaM Code fitting theoretical spectra of water bands to the measured ones using a chi-square function [12]. Spectra were taken during the total combustion time. As face value, the maximum temperature of the total combustion process was used.

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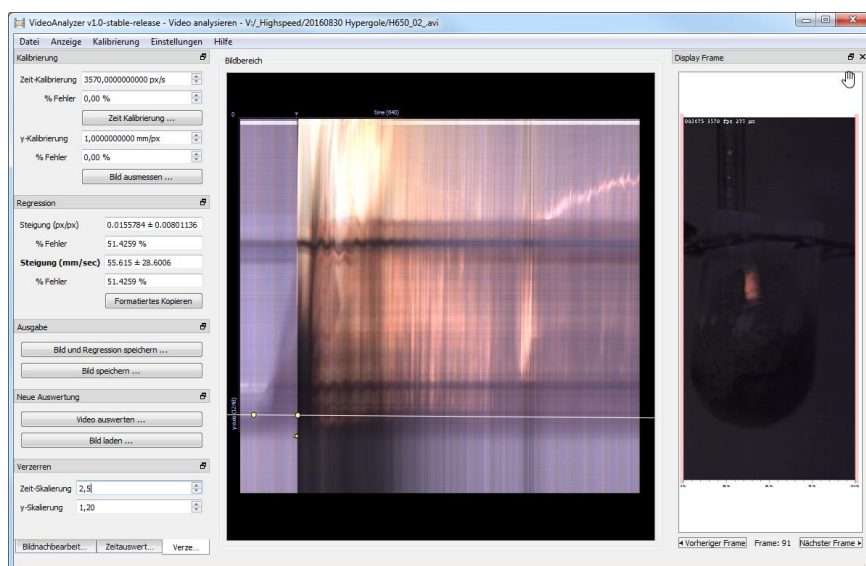Figure 3 Experimental set-up to investigate hypergolic behavior of the investigated bi-propellants.

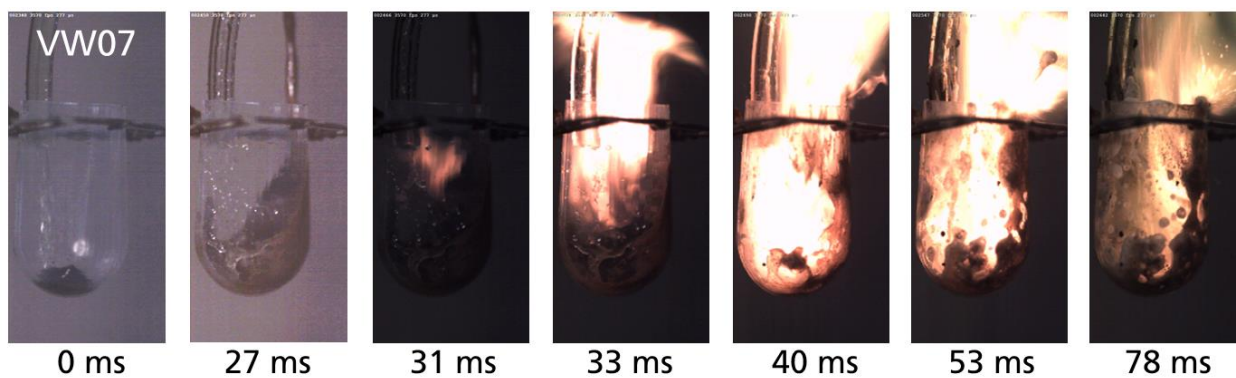Figure 4 Screen shot of ICT-video-analyzer to determine ignition delay time.

Figure 5 Selected frames with characteristic moments of the ignition and combustion sequence.

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4. Results

All oxidizer-fuel combinations result in a hypergolic reaction with AMIM DCA. Figure 6 shows still frames taken from the high-speed movies. Most propellant combinations ignited spontaneously. Hydrogen peroxide with a purity of 70% ignited only in a pale flame, but most others generated a bright flame except of Ox AN 1 to Ox AN 4, which only decompose with strong smoke formation. In general, the reaction using oxidizer solutions only including AN (Ox AN 9) and HSPO usually burnt less intensive as solutions with ADN (VW10 and VW15).

$H_2O_2(70\%)$ $H_2O_2(94,7\%)$ Ox AN 9   Ox AN 15   VW10   VW15
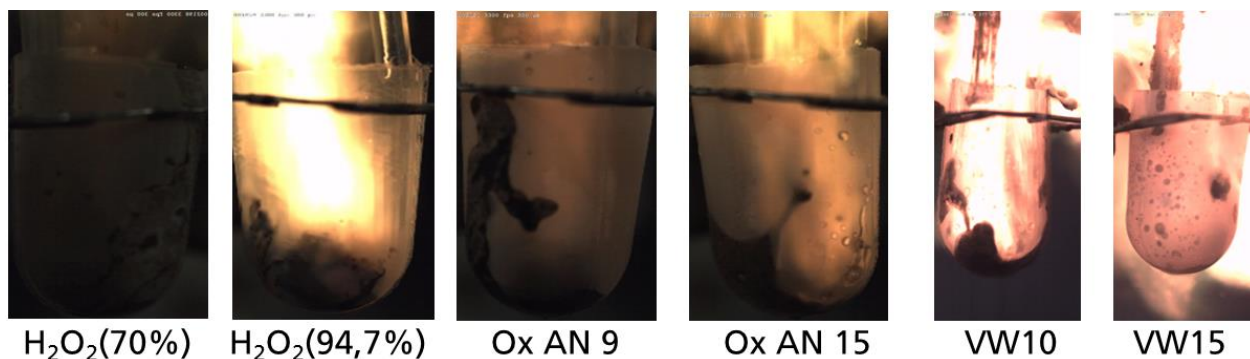
Figure 6: Hypergolic reaction of selected oxidizers with AMIM DCA.

The ignition delay times received from all tests are listed in Table 2 ordered by oxidizer. The values range from 9 ms to nearly 200 ms. With respect to the applied simple experimental set-up, which causes poor mixing before ignition with high heat loss, these values appear still sufficient for a rocket propulsion application. In a rocket motor, the mixing process will be extensively optimized to achieve significantly reduced ignition delay times.

The physical factors mentioned above may delay the ignition, but no meaningful reason for pre-ignition was recognized. Therefore as already mentioned, the shortest results were identified as experimental ignition delay times for further discussion.

High-concentrated hydrogen peroxide (purity 94.7%) ignites fastest within less than 10 ms. Hydrogen peroxide with 70% purity ignites after about 70 ms. This is the order of magnitude of most oxidizers including solved salts. Only the oxidizers with high water content JH Ox. 3 including 15% AN and 14/125 including 15% ADN ignited significantly slower after 192 ms and 161 ms. Increasing the content of ADN to 20% (14/124) shortens the ignition delay time to 86 ms. On this observation, it is remarkable that Ox AN 1 to Ox AN 4 produced from more pure hydrogen peroxide and including a higher salt concentration of 29% did not ignite under the same conditions. In general, oxidizer solutions containing high hydrogen peroxide purity or ADN amount (VWxx series) of more than 10% react significantly faster with ignition delay times <30 ms.

In Figure 7, the ignition delay times are plotted versus hydrogen peroxide purity (a), oxygen balance (b), adiabatic temperature of the pure oxidizer (c) and the adiabatic combustion temperature of the bi-propellant reaction (d). The color and shape of the dots correspond to the type of solved materials as specified in the legends.

The ignition delay time correlates fairly well with the inverse of the purity of hydrogen peroxide as depicted in Figure 7a. Only some oxidizer solutions including AN and urea hydrogen peroxide (HSPO) tend to higher ignition delay times. A correlation with the oxygen balance Figure 7b is smoother and indicates shortest ignition delay times for high oxygen balance.

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Table 2 Ignition delay time (shortest value) and flame temperature (maximum value derived from water band analysis) of each test.

Oxidizer	Ignition delay time	Hottest flame temperature
	ms	K
H_2O_2 94.7%	9	2498
H_2O_2 90%	11	2286
H_2O_2 80%	22	2105
H_2O_2 70%	66	1911
JH Ox. 3	192	1773
14/124	86	1852
14/125	161	1775
Ox AN 1	(only smoke)	-
Ox AN 2	(only smoke)	-
Ox AN 3	(only smoke)	-
Ox AN 4	(only smoke)	-
Ox AN 5	127	1981
Ox AN 6	87	2120
Ox AN 7	71	2047
Ox AN 8	85	2116
Ox AN 9	71	2082
Ox AN 10	66	2110
Ox AN 11	105	2028
Ox AN 12	83	2084
Ox AN 15	93	2183
Ox AN 16	72	2133
VW04	20	2227
VW05	18	2126
VW06	26	2220
VW07	25	2197
VW08	35	1905
VW09	39	2121
VW10	48	2227
VW11	48	2130
VW12	58	1925
VW13	66	1970
VW14	56	2096
VW15	66	2117
VW16	25	2186
VW17	36	2125
VW18	70	2057
VW19	27	2133
VW20	32	2133

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As shown in Figure 7c, there is also a weak trend to shorter ignition delay times with higher adiabatic temperature of the oxidizer solution (calculated as monopropellant). But the correlation with this property is less strong as the other ones. This is surprising because usually it would be plausible that the exothermic decomposition of hydrogen peroxide would initiate and accelerate the hypergolic ignition. This is in a very good agreement with pure hydrogen peroxide (black dots) and also with pure solutions of ADN. But with solutes of AN and HSPO this trend is less significant. Finally the ignition delay time also correlates significantly inversely with the adiabatic temperature or better the heat release of the total bi-propellant reaction. Interestingly, the pure hydrogen peroxide ignites faster as the oxidizers including solutes. The hypergolic reaction will be initiated by the exothermal decomposition of hydrogen peroxide which is catalyzed by the fuel ingredients. The delayed decomposition caused by the solutes can be a hint for a stabilizing effect of these solved materials.
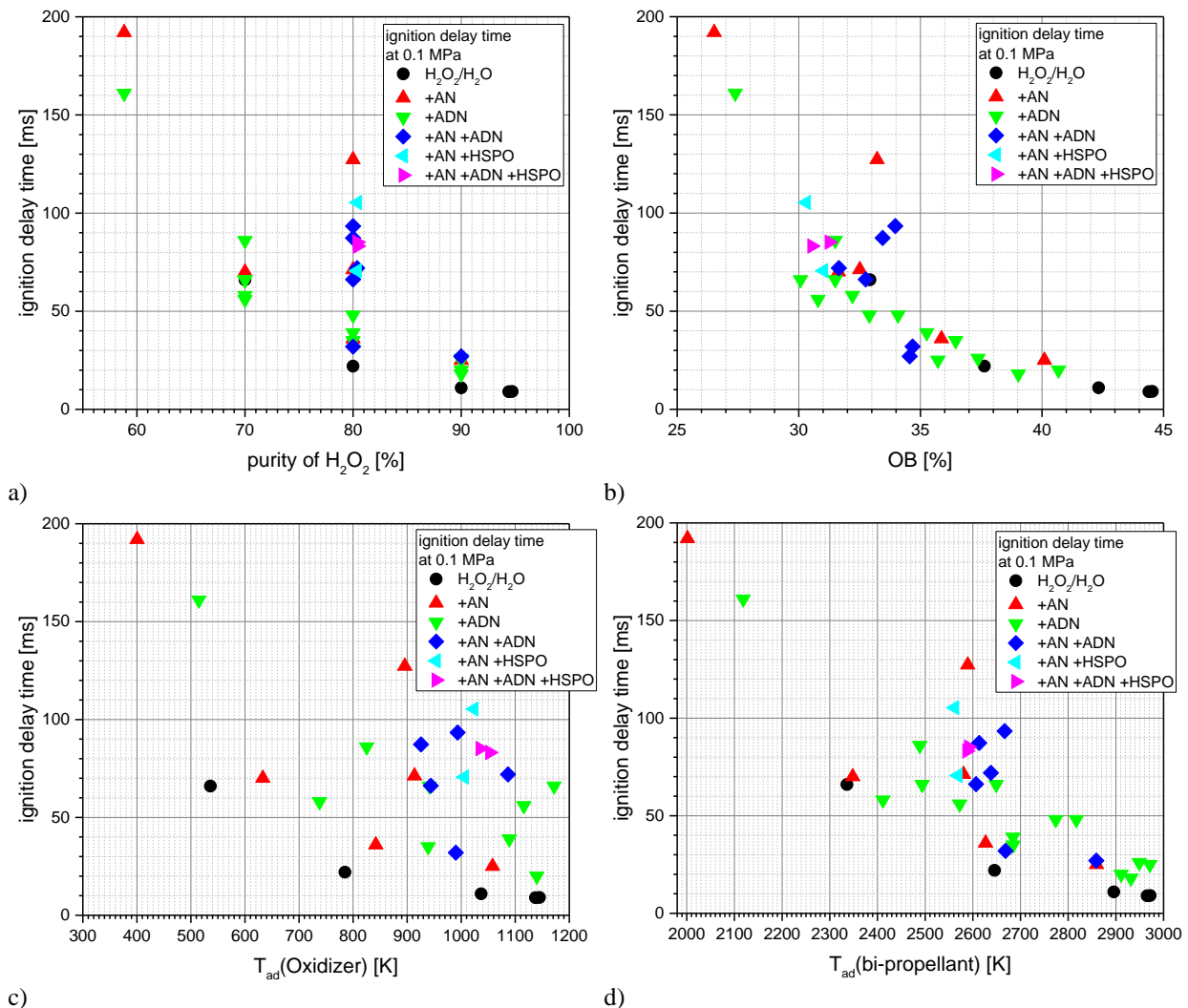
Figure 7 Ignition delay time (shortest values) of all tested oxidizers with AMIM DCA: Correlation with a) purity of hydrogen peroxide in oxidizer mixture, b) oxygen balance of oxidizer mixture, c) adiabatic decomposition temperature of the oxidizer mixture, d) adiabatic reaction temperature of bi-propellant reaction.

Measured flame temperatures correlate to the caloric values of the bi-propellant system which is indicated by the adiabatic temperature. So Figure 8 plots the maximum values of each sample versus the adiabatic temperature of the oxidizer-fuel reaction discriminated according to the components of the oxidizer solutes in hydrogen peroxide. Highest temperatures are achieved with high-concentrated hydrogen peroxide (purity 94.7%) with values close to 2500 K. The combinations including additives basing on less pure hydrogen peroxide feature in lower temperatures. In general, there is a conform correlation between the measured flame temperature and the predicted adiabatic one. Measured flame temperatures correlate to the caloric values of the bi-propellants indicated by the adiabatic temperature.

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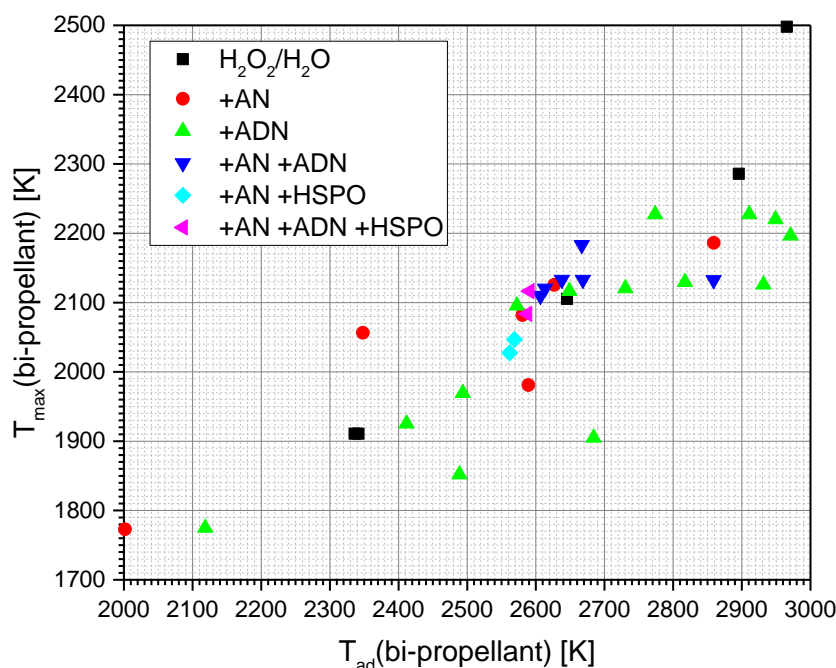

Figure 8 Maximum flame temperatures of the studied bi-propellant formulations measured using NIR-spectrometry versus adiabatic temperature calculated with ICT-Thermodynamic Code.

5. Conclusions

Hypergolic reactions with an energetic ionic liquid as fuel (basing on AMIM DCA) were investigated with solutions of ADN, AN and urea hydrogen peroxide in high-concentrated hydrogen peroxide of 70 to 90% purity. Applying small scale tests ignition delay times of 15 to 200 ms were received. Considering the simple experimental conditions causing strong heat loss this appear to be acceptable for rocket or satellite propulsion applications. Especially oxidizer solutions including high ADN concentrations result in short ignition delay times and high specific impulse of the bi-propellant reaction. Such solutions feature in low melting or glass transition points. Urea hydrogen peroxide may be used to reduce the glass transition but has an adverse influence to the performance and long-term stability. Significant inverse correlations of the ignition delay time with the oxygen balance and the performance of the bi-propellant system (characterized by the adiabatic temperature) maybe a helpful tool to develop or to optimize hypergolic propellant formulations.

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