Design, Construction and Comissioning of a Reaction Chamber for Hypergolic Fuels as well as first Optical Measurements of the Flame Emission

Konstruktion, Aufbau und Inbetriebnahme einer Reaktorkammer für hypergole Treibstoffe sowie erste optische Messungen der Flammenemission

> Master's Thesis by cand. aer. Jakob Balkenhohl IRS-19-S-056

Supervisor: Prof. Dr.-Ing. Stefan Schlechtriem Dr. Robert Stützer M.Sc. Felix Lauck

Deutsches Zentrum für Luft- und Raumfahrt, Institut für Raumfahrtantriebe

> Institut für Raumfahrtsysteme, Universität Stuttgart December 2019



UNIVERSITÄT STUTTGART **INSTITUTE OF SPACE SYSTEMS**



Pfaffenwaldring 29 · 70569 Stuttgart · Phone +49 (0) 711 685-62375 · Fax: +49 (0) 711 685-63596 · www.irs.uni-stuttgart.de

Master Thesis Work

of Mr. Balkenhohl, Jakob

Konstruktion, Aufbau und Inbetriebnahme einer Reaktorkammer für hypergole Treibstoffe sowie erste optische Messungen der Flammenemission

Design, construction and commissioning of a reaction chamber for hypergolic propellants as well as first optical measurements of the flame emission

Motivation:

For decades, liquid hypergolic fuel-oxidizer combinations have been used in space to propel space vehicles. The most commonly used propellants consist of hydrazine (N_2H_4) or one of its derivatives as a fuel and dinitrogen tetroxide (N_2O_4) as an oxidizer. When the two components of the propellant come into contact, spontaneous ignition occurs after a short time period. This feature is called hypergolic. Its advantages are that no external ignition source is required and ignition takes place reliably and reproducibly. The disadvantages of these fuels are that they are toxic and carcinogenic. The oxidizer is also toxic and highly corrosive. Due to these negative properties, handling of those propellants is very complex and expensive. For this reason, research is being carried out into novel alternative propellants, so-called "green propellants". These are characterized by the fact that they are less toxic and therefore easier to handle.

So far, only few details are known on the hypergolic ignition process and the combustion of conventional and especially novel fuels, such as ongoing chemical reactions and intermediate products. Within the scope of this work, a reaction chamber is to be designed and manufactured in which conventional fuels can be safely handled and tested. In this reaction chamber, hypergolic ignition tests of conventional and novel propellants will be carried out. The ignition process and ignition delay time is to be observed with the aid of a high-speed camera. In addition, the spectral distribution of the flame emission is to be measured.

Tasks:

- Familiarization with the topic of hypergolic propellants, the ignition behavior of hypergolic propellants and possibilities for determining the ignition delay of hypergolic propellants.
- Identification of requirements and boundary conditions for a suitable reaction chamber for hypergolic 0 ignition tests with conventional and novel fuels
- Design and assembly of the reaction chamber .
- Set-up and calibration of measurement technology
- Performing experiments with hypergolic propellants
- Evaluation of the measurement data and documentation of the results

Supervisor:	Dr.	Robert	Stützer,	Felix	Lauck
Jupervisor.	01.	nobere	Junizery	I Clix	Laadi

29.05.2019

Submission until:

Starting date:

29.11.2019 Prof. Dr. S. Schlechtriem

(Responsible Professor)

Acknowledgement of receipt: I hereby confirm that I read and understood the task of the master thesis, the juridical regulations as well as the study- and exam regulations.

Signature of the student

Legal Restrictions: The author/s of the master thesis is/are not entitled to make any work and research results which he/she receives in the process of writing this thesis accessible to third parties without the permission of the named supervisors. The author/s shall respect restrictions related to research results for which copyright and related rights already exist (Federal Law Gazette I / S. 1273, Copyright Protection Act of 09.09.1965). The author has the right to publish his/her findings as long as they incorporate no findings from the supervising institutions and companies for which restrictions exist. The author must consider the rules and exam regulations issued by the university and faculty of the branch of study where the master thesis was completed.

IRS Professors and Associate Professors:

Prof. Dr.-Ing. Stefanos Fasoulas (Managing Director) · Prof. Dr.-Ing. Sabine Klinkner (Deputy Director) · Prof. Dr. rer. nat. Alfred Krabbe · (Deputy Director) · Hon.-Prof. Dr.-Ing. Jens Eickhoff · Prof. Dr. rer. nat. Reinhold Ewald · PD Dr.-Ing, Georg Herdrich · Hon.-Prof. Dr. Volker Liebig · Prof. Dr.-Ing, Stefan Schlechtriem · PD Dr.-Ing, Ralf Srama

Erklärungen

Hiermit versichere ich, Jakob Balkenhohl, dass ich diese Masterarbeit selbstständig mit Unterstützung des Betreuers/der Betreuer angefertigt und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe. Die Arbeit oder wesentliche Bestandteile davon sind weder an dieser noch an einer anderen Bildungseinrichtung bereits zur Erlangung eines Abschlusses eingereicht worden.

Ich erkläre weiterhin, bei der Erstellung der Arbeit die einschlägigen Bestimmungen zum Urheberschutz fremder Beiträge entsprechend den Regeln guter wissenschaftlicher Praxis¹ eingehalten zu haben. Soweit meine Arbeit fremde Beiträge (z.B. Bilder, Zeichnungen, Textpassagen etc.) enthält, habe ich diese Beiträge als solche gekennzeichnet (Zitat, Quellenangabe) und eventuell erforderlich gewordene Zustimmungen der Urheber zur Nutzung dieser Beiträge in meiner Arbeit eingeholt. Mir ist bekannt, dass ich im Falle einer schuldhaften Verletzung dieser Pflichten die daraus entstehenden Konsequenzen zu tragen habe.

Ort, Datum, Unterschrift

Hiermit erkläre ich mich damit einverstanden, dass meine Masterarbeit zum Thema:

Konstruktion, Aufbau und Inbetriebnahme einer Reaktorkammer für hypergole Treibstoffe sowie erste optische Messungen der Flammenemission

in der Institutsbibliothek des Instituts für Raumfahrtsysteme ohne Sperrfrist öffentlich zugänglich aufbewahrt und die Arbeit auf der Institutswebseite sowie im Online-Katalog der Universitätsbibliothek erfasst wird. Letzteres bedeutet eine dauerhafte, weltweite Sichtbarkeit der bibliographischen Daten der Arbeit (Titel, Autor, Erscheinungsjahr, etc.).

Nach Abschluss der Arbeit werde ich zu diesem Zweck meinem Betreuer neben dem Prüfexemplar eine weitere gedruckte sowie eine digitale Fassung übergeben.

Der Universität Stuttgart übertrage ich das Eigentum an diesen zusätzlichen Fassungen und räume dem Institut für Raumfahrtsysteme an dieser Arbeit und an den im Rahmen dieser Arbeit von mir erzeugten Arbeitsergebnissen ein kostenloses, zeitlich und örtlich unbeschränktes, einfaches Nutzungsrecht für Zwecke der Forschung und der Lehre ein. Falls in Zusammenhang mit der Arbeit Nutzungsrechtsvereinbarungen des Instituts mit Dritten bestehen, gelten diese Vereinbarungen auch für die im Rahmen dieser Arbeit entstandenen Arbeitsergebnisse.

Ort, Datum, Unterschrift

¹Nachzulesen in den DFG-Empfehlungen zur "Sicherung guter wissenschaftlicher Praxis" bzw. in der Satzung der Universität Stuttgart zur "Sicherung der Integrität wissenschaftlicher Praxis und zum Umgang mit Fehlverhalten in der Wissenschaft"

Danksagung

Ich möchte mich an dieser Stelle bei allen Kollegen*innen bedanken, die mich bei der Erstellung dieser Arbeit im Rahmen meiner Tätigkeit am M11 des Instituts für Raumfahrtantriebe am DLR-Lampoldshausen unterstützt haben.

An erster Stelle gilt mein Dank Herrn Prof. Dr. Schlechtriem, Leiter des Instituts für Raumfahrtantriebe, der die Durchführung dieser Arbeit überhaupt erst ermöglicht hat. Ein besonderer Dank gilt zudem meinen beiden Betreuern, Herrn Felix Lauck M.Sc. und Herrn Dr. Robert Stützer, die mich stets in meiner Arbeit unterstützt haben und mit Rat und Tat zur Seite standen.

Außerdem möchte ich mich bei Herrn Dr. Dominic Freudenmann und allen Kollegen im Chemielabor für die Bereitstellung des Laborarbeitsplatzes bedanken. Schließlich sei dem gesamtem Team am M11 gedankt. Ich werde die gute Arbeitsatmosphäre und Hilfbereitschaft Aller vermissen.

Abstract

Hypergolic propellants are fuel-oxidizer pairs that have been used in spaceflight engines since the 1960s and are characterized by their property of self-igniting upon contact. At the Institute of Space Propulsion of the German Aerospace Center (DLR), research is being conducted on novel green hypergolic propellants that are to replace notoriously toxic conventional fuels such as monomethylhydrazine (MMH) and nitrogen tetroxide (NTO). More specifically, highly concentrated hydrogen peroxide (HTP) in combination with ionic liquids (ILs) are being looked into as promising candidates.

In the scope of this thesis, a test bench was designed and implemented that easily and reliably allows to perform drop-tests with hypergolic propellants in an enclosed chamber. This allows for the classification of conventional as well as novel green propellants with respect to their ignition delay time and ignition behavior in general. The ignition delay time (IDT) is defined as the time between contact of both the components and first appearance of a flame, and is an important characteristic of hypergolic propellants. High speed video imaging was employed to determine the IDT and analyze the combustion regime. Additionally, the possibility of performing flame emission diagnostics through optical spectroscopy was implemented. This allowed to further analyze the combustion and yield information on intermediate products and flame temperature. The HYPED UP (HYPergolic Drop-Test SetUP) test bench was successfully put into operation and more than 150 drop tests with HTP and an ionic liquid at varying test conditions were performed. The impact of different factors such as drop size and height on the IDT was analyzed. A copper additive was dissolved in the IL as a catalyst. An added 5 wt% decreased the average IDT from 31.3 ± 3.8 ms to 13.3 ± 1.1 ms. Strong alkali metal doublets of sodium and potassium were measured in the spectra. In the OH spectral band at around 306 nm, a correlation between flame temperature and emission peak intensity was observed.

Zusammenfassung

Hypergole Treibstoffe sind Kombinationen von einem Oxidator und einem Brennstoff, die seit den 1960er Jahren in Raumfahrtantrieben eingesetzt werden und sich durch ihre Eigenschaft auszeichnen, bei Kontakt spontan zu reagieren. Am Institut für Raumfahrtantriebe des Deutschen Zentrums für Luft- und Raumfahrt werden neuartige grüne hypergole Treibstoffe erforscht, die toxische konventionelle Treibstoffe wie Monomethylhydrazin (MMH) und Stickstofftetroxid (NTO) ersetzen sollen. Genauer gesagt, werden hochkonzentriertes Wasserstoffperoxid (HTP) in Kombination mit ionischen Liquiden (ILs) als vielversprechende Kandidaten untersucht.

Im Rahmen dieser Arbeit wurde ein Prüfstand konzipiert und implementiert, der es ermöglicht, einfach und zuverlässig Tropftests mit hypergolen Treibstoffen in einer geschlossenen Kammer durchzuführen. Dies ermöglicht die Klassifizierung von konventionellen und neuartigen grünen Treibstoffen hinsichtlich ihres Zündverzugs und ihres Zündverhaltens im Allgemeinen. Der Zündverzug (ZV) ist definiert als die Zeit zwischen dem ersten Kontakt der Komponenten und dem ersten Auftreten einer Flamme und ist ein wichtiges Merkmal von hypergolen Treibstoffen. Zur Bestimmung des ZV und zur Analyse des Verbrennungsregimes wurde eine Hochgeschwindigkeitskamera eingesetzt. Zusätzlich wurde die Möglichkeit der Flammenemissionsdiagnostik durch optische Spektroskopie implementiert. Dies ermöglicht weitere Analyse der Verbrennung und liefert Informationen über Zwischenprodukte und die Flammentemperatur.

Der HYPED UP (HYPergolic Drop-Test SetUP) Prüfstand wurde erfolgreich in Betrieb genommen und mehr als 150 Tropf-Tests mit HTP und einem ionischen Liquid unter unterschiedlichen Prüfbedingungen wurden durchgeführt. Der Einfluss verschiedener Faktoren wie Tropfengröße und -höhe auf den ZV wurde untersucht. Ein Kupfer Additiv wurde in dem IL als Katalysator gelöst. Ein Additiv von 5 Gew.-% verringerte den durchschnittlichen ZV von $31,3 \pm 3$ ms auf $13,3 \pm 1$ ms. Starke Alkalimetall Doppellinien von Natrium und Kalium wurden in den Spektren gemessen. Im OH-Spektralband bei etwa 306 nm wurde eine Korrelation zwischen Flammentemperatur und der Intensität der Emissionspeaks beobachtet.

Contents

Li	List of Figures II		
Li	st of	Tables	v
N	omen	Inclature	VI
1	Intr	oduction	1
2	The	eoretical Background	3
	2.1	Hypergolic Ignition	3
		2.1.1 Fundamentals	3
		2.1.2 Ignition Behavior and Ignition Delay Time	4
		2.1.3 Hypergolic Hydrogen Peroxide based 'Green Propellants'	5
	2.2	The Drop-Test Method	6
		2.2.1 Existing Setups	7
		2.2.2 Setup for this Thesis \ldots	8
	2.3	Optical Spectroscopy	9
		2.3.1 Atomic and Molecular Spectra	9
		2.3.2 Flame Emission Spectroscopy	10
		2.3.3 Czerny-Turner Spectrometer	11
3	Cha	imber Design	13
	3.1	Design Driving Requirements and Conditions	13
	3.2	Design and Construction of the chamber	13
		3.2.1 Chemical Compatibility and Resistance	15
		3.2.2 The Basic Chamber Design	15
		3.2.3 Window Material and Thickness	17
		3.2.4 Mounting and Sealing of the Windows	18
		3.2.5 Drop System	20
4	Test	t Bench Setup and Calibration	22
	4.1	Subsystem A: Measurement and Test Controlling	22
		4.1.1 Syringe Pump and Cleaning System	23
		4.1.2 Temperature and Pressure Measurement	24
		4.1.3 LabVIEW Routine and User Interface	26
	4.2	Subsystem B: High Speed Recording	26
	4.3	Subsystem C: Spectroscopy	28
		4.3.1 Software for System Configuration and Data Acquisition	30
		4.3.2 Wavelength or X-axis Calibration	31
		4.3.3 Optical Fiber Alignment and Focus	32
		4.3.4 Device Curve Determination	33
		4.3.5 Gain Correction	33
		4.3.6 Trigger Handling	34
	4.4	Subsystem D: Atmosphere Regulation	36
	4.5	Further Preliminary Setup Investigations	36

	4.6	HYPED UP Test Bench and Setup Procedure	36
5	Exp(5.1 5.2 5.3	erimental Procedure and Data analysisExperimental Procedure	 38 38 39 41 41 42 42 42 44
6	Test 6.1 6.2 6.3	Results and Discussion Preliminary Pressure Tests Delay Time Determination and Combustion Analysis Spectroscopy 6.3.1 Spectra Slit Width Influence 6.3.2 Comparing Flame Emission Spectra 6.3.3 OH Band	46 46 53 53 53 53
7	Summary and Outlook 58		58
Bi	Bibliography		
8	B Deutsche Zusammenfassung		64
9	Арр	endix	66

List of Figures

1.1	A simple drop-test setup	1
2.1	Qualitative illustration of the change of temperature over time in a hypergolic reaction [5]	4
22	Chart showing off the different ways HP can be used as a propellant	5
$\frac{2.2}{2.3}$	The HVPERTESTER dron-test setup at Purdue University [18]	8
$\frac{2.5}{2.4}$	Drop test setup at the Center of Space Technologies in Warsaw [10]	8
2.4 2.5	The Balmer series of the Bohr model for hydrogen including the resulting wave-	0
2.0	lengths for different transitions to the ground state $n = 2$ [25]	10
26	Illustration of a molecular energy level diagram with electronic vibrational and	10
2.0	rotational levels [23]	10
27	OH visualisation in a $LOX/H2$ spray	11
2.1	Spectral applysis of the OH Band	11
2.0	Top view drawing of the optical path in a Czerny Turner Spectrometer [25]	11
2.9 2.10	Crating curves for different blaze wevelengths [37]	11 19
2.10	Grating curves for different blaze wavelengths [57]	12
3.1	First conceptual sketch of the chamber design	14
3.2	Final chamber design	14
3.3	Basic CAD models of the three proposed chamber designs	15
3.4	3D model of sealing concept at the tube ends	16
3.5	3D model showing the removable side panel	17
3.6	Transmission wavelength range for different optical substrates [44]	18
3.7	Window mount concept	19
3.8	Cross section of the window clamped down onto the chamber side	19
3.9	The final design of the syringe pump	20
3.10	Step-by-step illustration of the cleaning system	21
3.11	Close-up of the implemented system	21
4 1	Concentral illustration of the UNDED UD toot hand, and its different colorestance	00
4.1	Conceptual inustration of the HYPED UP test bench and its different subsystems	22
4.2	Conceptual wiring diagram of 4 phase unipolar stepper motor	20 02
4.5	Wining diagram of the surings nump and cleaning system	20 94
4.4	Wiring diagram of the DP2102 program transducer	24
4.5	A generalized of the HVDED UD LabVIEW front papel	20
4.0	A screenshot of the appropriate of the apportunity and subsystem	21
4.1	SChematic of the components of the spectroscopy subsystem	20
4.0	Efficiency curves of the CCD and Intensifier as well as the combined curve	29 20
4.9	From the raw CCD image to the intensity plot	29
4.10	The acquired spectra of the $Hg(\Lambda r)$ calibration lamp for two different gratings	30
4.11	with peak locations	21
1 19	Optical collimator setup	25 91
4.12 / 19	Device curve determination	- วว - २∄
4.10 / 1/	The determined intensity values for different gains as well as the exponential fit	94 25
4.14 / 15	Timing diagram for continuous spectra recording using a pulse generator	25 25
4.10	r ming magram for continuous spectra recording using a pulse generator	55

$4.16 \\ 4.17$	The HYPEDUP test bench	$\frac{36}{37}$
5.1 5.2	Plots showcasing the different data processing steps	40 42
$5.3 \\ 5.4$	Data acquired from video screenshots for drop size and speed determination	43 44
$6.1 \\ 6.2$	Image series capturing hypergolic ignition between HTP and EMIM SCN \dots Image series capturing hypergolic ignition between HTP and EMIM SCN + 1	48
6.3	wt% CuSCN	49
6.4	wt% CuSCN	50 50
$\begin{array}{c} 6.5 \\ 6.6 \end{array}$	The resulting IDT averages for the different test variations	$\frac{51}{52}$
$\begin{array}{c} 6.7 \\ 6.8 \end{array}$	The same spectra recorded with three different slit widths	$53 \\ 54$
$6.9 \\ 6.10$	The Na-doublet recorded with the three gratings	$54 \\ 55$
6.11 6.12	Li-doublet, non resolved	55 5 <i>c</i>
$6.12 \\ 6.13$	Comparism of recorded and simulated highly-resolved OH band	$\frac{50}{56}$
$6.14 \\ 6.15$	Comparism of recorded spectra with external experimental data OH Band of ignition between HTP and EMIM SCN with varying wt% of Cu	57
	catalyst	57
9.1	Acquired spectra of Hg(Ar) lamp with 600 g/mm grating $\ldots \ldots \ldots \ldots \ldots$	66

List of Tables

4.1	Calibrated coefficients of the pressure transducer	25
4.2	Gratings of the spectrometer and the resulting linear dispersion and coverage [37]	28
4.3	Emission lines from literature and the measured lines using the three available	
	gratings	32
5.1	The structure of a typical obtained spectral data $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	39
6.1	Test matrix showing the different variations that were tested	46
6.2	The determined drop sizes	47
6.3	Results of the baseline test	47
6.4	Results for variation of the drop order	48
6.5	Results for variation of the oxidizer to fuel ratio	49
6.6	Results for varying Cu catalyst proportions	51
6.7	Results for variation of drop height	51
6.8	Literature and measured spectroscopic data of alkali fluorescence lines	55
6.9	Literature and measured spectroscopic data of copper lines	55
6.10	The relative intensity of peak G_1 in the OH bands $\ldots \ldots \ldots \ldots \ldots \ldots$	56
7.1	Influence of test parameters on IDT	59
8.1	Einfluss der getesteten Parameter auf den Zündverzug	65

Nomenclature

Acronyms

a.u.	arbitrary unit
BNC	Bayonet Neill Concelman
CCD	charged coupled device
\mathbf{CF}	conversion factor
CW	central wavelength
DC	Direct Current
DLR	Deutsches Luft- und Raumfahrtzentrum
FES	flame emission spectroscopy
FKM	fluproelastomer
fps	frames per second
HTP	High-test peroxide
I/O	Input/Output
IRNA	inhibited red fuming nitrid acid
IDT	ignition ielay time
IL	ionic liquid
LOX	liquid oxygen
MMH	nonomethyl hydrazine
NTO	nitrogenetetroxide
REACH	Registration, Evaluation, Authorization of Chemicals
RPM	revolutions per minute
SCAPE	Self-Contained Atmospheric Protective Ensemble
SD	standard deviation
TTL	transistor-transistor logic
UDMH	unsymmetrical dimethyl hydrazine
UV	ultraviolet
WFNA	white fuming nitrid acid
ZV	Zündverzug

Greek Symbols

β	[°]	diffraction angle
Δ	[-]	difference
Δ_{App}	[nm]	apparatus function
λ	[nm] or [Å]	Wavelength
ν	[1/s]	frequency
σ	[-]	uncertainty
$ au_{chem}$	[ms]	chemical delay time
$ au_{ign}$	[ms]	ignition delay time
$ au_{phys}$	[ms]	physical delay time
$egin{array}{lll} \lambda & & \ u & & \ abla & \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	[nm] or [Å] [1/s] [-] [ms] [ms] [ms]	Wavelength frequency uncertainty chemical delay tin ignition delay tin physical delay tin

Latin Symbols

c'	[m/s]	speed of light
D	[mm or px]	diameter

Ε	[J]	energy
Eq_m	$[N/mm^2]$	E-module
\mathbf{F}_{a}	[-]	elastic limit
f	[m]	focal length
GRT	[g/mm]	grating
h	[Js]	Planck's constant
Ι	[-]	intensity
I_{sp}	$[\mathbf{s}]$	specific impulse
k	[-]	groove distance
Κ	[-]	empirical constant
m	[-]	order
n	[-]	energy level
р	[bar]	pressure
R	[-]	spectral resolution
s	[-]	standard deviation
\overline{s}	[-]	confidence interval
\mathbf{S}_F	[-]	safety factor
t	[mm]	thickness
Т	[K]	temperature
u	[m/s]	velocity
U	[V]	voltage
V	[µl]	volume
$\mathrm{wt}\%$	[-]	weight percent

Indices

0	impact
1	first ignition event
2	second ignition event
*	radical
b	bowl
d	drop
i	ignition
\sup	supply
v	vaporization

1 Introduction

Hypergolic propellants, which are pairs of oxidizer and fuel that ignite spontaneously upon contact, have been used in spaceflight since the early 1960s. In absence of an additional ignition system, rocket engines using this type of propellant are typically less complex and subsequently more reliable in both design and operation than their non-hypergolic counterparts. This, together with their good storability, makes them optimal for long term missions such as maneuvering systems on deep-space missions.

As the space industry gradually moves away from the early exploration Apollo days, where costs were only secondary and environmental protection was not yet prioritized, the focus has now shifted towards the reduction of both costs as well as the harmful impact of propellants on the environment. Conventional hypergolic fuels such as monomethylhydrazine (MMH) and nitrogen tetroxide (NTO), however, are notoriously toxic and harmful to both humans and the environment, thus requiring a significant amount of effort and special equipment to be handled in a safe manner. This drives up the costs.

At the Institute for Space Propulsion of the German Aerospace Center (DLR) in Lampoldshausen, as well as other places, research is being done on the discovery and classification of novel alternative 'green' hypergolic propellants that perform in a similar way to conventional fuels, while simultaneously being less toxic and thus less environmentally damaging as well as cheaper in handling. One category of such green propellants are ionic liquids in combination with highly concentrated hydrogen peroxide (HTP). A common and rather simple method of testing if a combination is hypergolic and getting a first estimate of its reactivity is the 'drop-test' method.



FIGURE 1.1: A simple drop-test setup

As can be seen in Figure 1.1, in its most simple form one component is dropped onto the other. Typically, the ignition delay time (IDT), that is the time between impact of the two components and ignition, is determined using a high speed camera. Generally speaking, a low IDT is desired as it prevents a hard start that could potentially destroy the engine.

Due to the highly complicated and intricate nature of hypergolic ignition, a wide array of factors

have an effect on its behavior and characteristics. In general, the exact processes of the ignition remain unclear and have not been analyzed in-depth for HTP and IL combinations. The overall goal of this thesis is to design, construct and assemble a drop-test chamber and test bench that allows to reliably test both conventional as well as novel hypergolic fuel-oxidizer combinations. The setup should keep as many of the factors that impact the IDT constant as possible and allow to purposefully change some to analyze its impact on ignition. Apart from high-speed imaging, the chamber is too allow for performance of flame emission spectroscopy (FES), that is spectral analysis of the flame. By doing so, information on the different chemical reactions taking place during ignition as well as intermediate products can be found. Finally, the correct functionality of the system is to be tested by performing a number of tests with different conditions.

Organization

This thesis can roughly be divided into 5 main sections. The second chapter covers the necessary theoretical background needed to properly evaluate and understand the thesis. The third chapter goes into detail on the requirements the chamber needs to fulfill and the design that follows. Chapter four discusses the setting up of the entire test bench and its subsystems as a whole. In the fifth chapter, the experimental procedure and data analysis is explained. The sixth chapter presents the results of the first tests. Finally, a summary and an outlook is given.

2 Theoretical Background

The following chapter covers the theoretical groundwork necessary for the better understanding of the topic off this thesis. Starting off, the phenomenon of hypergolicy as well as its ignition behavior is elaborated upon. Continuing, the drop-test setup is described in more detail and a brief overview of already existing setups is given. After that, hydrogen peroxide as a propellant in general as well as in combination with so called ionic liquids (ILs) is discussed. Finally, the physical background and general concept of flame emission spectroscopy is explained and an overview on the Czerny-Turner spectrometer is given.

2.1 Hypergolic Ignition

2.1.1 Fundamentals

As mentioned in the introduction, hypergolic propellants are oxidizer-fuel pairs with the unique feature of self-igniting upon contact. Common hypergolic fuels are based on hydrazine (N_2H_4) or its derivatives in combination with nitrogen tetroxide:

- Monomethylhydrazine MMH and NTO e.g. Apollo Command Module, Ariane 5 EPS.
- Aerozine 50 (50% unsymmetrical dimethyl hydrazine UMDH + 50% hydrazine) and NTO e.g. Apollo Lunar Module.
- UDMH and NTO e.g Ariane 1 1st and 2nd stage.

Other hypergolic fuels are methanol, triethylamine, anilinie, toludine and N-methyl aniline just to name a few. Other oxidizers are liquid oxygen, inhibited red and white fuming nitric acid (IRNA/WFNA) and hydrogen peroxide [1, 2]. Using this type of propellant in a bipropellant hypergolic engine has both advantages as well as disadvantages when compared to conventional ignition, where some sort of external energy input is required in order for ignition to occur.

As briefly mentioned in the introduction, its most obvious advantage is the elimination of an ignition system, which goes hand in hand with a less complex engine design. It is also what allows for re-ignition of the engine, making it well suited for upper stages or rockets of spacecrafts. Conventional hypergolic propellants are liquid and have good long-term storability. Therefore they are commonly used for large spacecraft such as the Automated Transfer Vehicle (ATV) and many geostationary satellites.

Apart from their advantages, all of the above mentioned hypergolic propellants typically used for space application have a major drawback - they are highly corrosive, toxic and volatile. This means they require the use of special suits such as the SCAPE (Self-Contained Atmospheric Protective Ensemble) and extreme care when being handled, as an accidental spill would immediately lead to contamination of the atmosphere. The resulting necessary precautions during production, transportation and storage of the substances drive up the costs. Furthermore, all materials in contact with the propellant must be chemically resistant and non-corroding. This excludes classical materials used in space technology such as aluminum alloys, stainless steel, titanium, copper or nickel [2]. As of 2011, hydrazine and its derivatives have been placed on the candidate list of substances of very high concern by the European REACH regulation due to its potentially carcinogenic effects [3]. This means its usage could be banned in the long run. The negative health implications combined with the high handling costs of the conventional propellants have created a demand for new, non-toxic 'green' hypergolic propellants.

2.1.2 Ignition Behavior and Ignition Delay Time

The ignition delay time τ_{ign} , or IDT for short, is defined as the time between first contact of the fuel and oxidizer and the ignition of the mixture of hypergolic propellants. Generally speaking, a small delay is desirable as it prevents the accumulation of a combustible mixture in the chamber which can lead to unwanted large pressure spikes and subsequential engine failure ('hard engine start'). However, a IDT that is too short could potentially damage the injector. Investigations on RFNA have shown that a smaller ignition delay time corresponds to a higher specific impulse I_{sp} [4].

The physical process behind hypergolic ignition is of a highly complex nature that requires a deeper understanding on its theoretical background. For this thesis, the focus will be put on a simplified qualitative analysis.

In general, in order for an ignitable gas phase to exist, the two liquid components need to mix, heat up and evaporate. Figure 2.1 qualitatively illustrates the change of temperature over time in a hypergolic reaction as well as the different steps along the way.



FIGURE 2.1: Qualitative illustration of the change of temperature over time in a hypergolic reaction [5]

From the moment of contact 0 to A, the two components mix. However, no chemical reaction takes place yet. As the fuel and oxidizer continue mixing, they begin to react. The energy dissipated in the exothermic chemical process heats up the liquid until preignition vapor starts forming (B). The continuously ongoing reactions further heat up the gaseous phase until ignition occurs at C. The temperature continues rising and the final combustion temperature is reached. The time from B, the initial vaporization of the mixture, to ignition at C is often referred to as the chemical delay time τ_{chem} , as the main processes occurring in that phase are of chemical nature. It is argued to be a better indicator of the hypergolic properties of the used substances as it eliminates the physical mixing factor. Sticking to that denotation, the time from O to B can be referred to as the physical delay time τ_{phys} , since in these phases the physical mixing processes are dominant. The sum of both results in the total ignition delay time IDT. Of course, in reality, neither of the phases are purely physical or chemical processes. [5, 6, 10]

The speed at which these different phases occur is greatly influenced by many different physical

and chemical factors. Physical factors are for example the amount of fuel and oxidizer used, how well they mix, the initial temperature of the substances and the test chamber, the shape of the chamber, the surrounding pressure, the volume of the gaseous phase compared to the volume of the chamber and so on. Chemical factors are of course the chemical composition of the involved substances and their respective reactivity.

There are a number of methods that can be used to determine the IDT, such as the droptest method, the method of impinging jets [7], the Pino method [8] or combustion in micro chambers [9]. In the scope of this thesis, a drop-test chamber is designed and constructed.

2.1.3 Hypergolic Hydrogen Peroxide based 'Green Propellants'

Hydrogen peroxide $(H_2O_2 \text{ or } HP)$ is a colorless an odorless non-flammable liquid. It has been utilized as a propellant in space flight since the 1940s, where it was first used in the engine of the German He-176 aircraft as a monopropellant decomposed by a catalyst [11]. When used as a propellant, highly concentrated hydrogen peroxide with concentrations higher 90% is typically desirable. It is then commonly referred to as high test peroxide (HTP) or rocket grade hydrogen peroxide (RGHP). The following illustration (fig. 2.2) shows the different ways in which HTP can be used as a propellant in rocket propulsion.



FIGURE 2.2: Chart showing off the different ways HP can be used as a propellant

When used as a monopropellant, the HTP is decomposed by a catalyst. As a bipropellant, it can act as an oxidizer either in liquid-liquid or in staged combustion. In staged combustion, the HTP is decomposed by a catalyst and fuel is then added into the resulting hot mix of oxygen and water. The area of application that is of interest for this thesis is its hypergolic property in liquid-liquid combustion (framed in red). Up until the last few decades, research on its usage as part of a hypergolic system was minimal [12]. However, due to its low toxicity properties and environmentally friendly decomposition products, HTP has moved back into research focus as a promising oxidizer in bipropellant rockets for novel 'green' hypergolic propellants. This is not to say that HTP is not dangerous. When handling HTP, absolute care and proper protection is necessary as it is still harmful to the eyes, skin and respiratory system. It is highly flammable in combination with fuel and can cause explosions. Contact with organic material can lead to self-ignition.

Focusing on HTPs hypergolic characteristics, there are liquid fuels that are intrinsically hypergolic with HTP. However, these are very rare. Instead, additives are dissolved in a fuel that is not hypergolic with HTP on its own. Depending on how the additive enables a hypergolic chemical reaction, a distinction is made between reaction driven and catalytically driven fuels [12, 13].

Catalytic hypergolic fuels are transition metallic salts dissolved in fuel. When mixed with HTP, the ion of the metal salt catalyzes the break-down of the HTP into hot gaseous oxygen and water vapor. The energy dissipated in that process then heats up the mixture until it vaporizes and, after an ignition delay, combusts together with the oxygen. The main disadvantage of these fuels is that the added metallic salts cause an increase in the average molecular weight, which in return reduces the exhaust velocity and specific impulse. An example of such a fuel is Block 0, a mixture of methanol and manganese acetate tetrahydrate developed by the U.S. Navy in the 1990s [14]. Other suitable cations for HTP are $\operatorname{Co}^{+2/+3}$, $\operatorname{Cu}^{+1/+2}$ or $\operatorname{Fe}^{+2/+3}$, just to name a few [15].

Reaction driven fuels contain an additive that exothermically reacts directly with the HTP rather than decomposing it. The consequence of this is a higher energy release, a faster fuel vaporization and consequentially lower ignition delays [13]. Reactive additives are typically a compound of light metals such as boron, lithium or aluminum. Reactive fuels can be enhanced even further by adding a catalyst.

Either way, these propellants need to fulfill a number of requirements to be considered a possible replacement of conventional fuels. Most importantly, they should have a high specific impulse, short ignition delay and good storability at a low cost.

Ionic Liquids

Some ionic liquids (ILs) fall into the category of reactive hypergolic fuels. Per definition, ILs are salts with a melting point below 100 °C that can be liquid at room temperature [16]. They consist of weekly linked organic or inorganic cations and anions [17], which leads to very low vapor pressures. This, together with their high thermal stability and high energy density, makes them a promising alternative fuel to hydrazine based fuels. Hypergolic ionic liquids with HTP have been investigated in the past. In general, the hypergolic properties of ILs mainly depend on the anion [16].

In the scope of this thesis, the ionic liquid 1-Ethyl-3-methyl-imidazolium-thiocyanate (EMIM SCN) with varying degrees of the transition metallic salt Copper(I)-thiocyanat (CuSCN) added as a catalyst was used as a fuel in combination with HTP to perform first measurements in the developed drop-test setup.

2.2 The Drop-Test Method

The drop-test method is debatably the simplest method that allows to test if a liquid fueloxidizer combination is hypergolic and obtain first ignition delay time values if this is the case. Another advantage is that it requires only minimal quantities of fuel and oxidizer. Its usage dates back to the 1930s, when hypergolicy was first discovered in Germany and a vast amount of tests were performed to find hypergolic oxidizer/fuel combinations. The IDT can be determined through different methods that all rely on some type of electronic equipment. Some of these methods are:

• A photodiode that detects the flash of luminosity at ignition and creates an electric signal.

- A microphone, piezo-sensor or velocity transducer under the liquid pool that detects the impact of the drop and creates an electric signal.
- Laser-photodiode combination that detects a drop-off in current coming from the diode when the drop passes through the laser beam.
- Pressure transducer that detects a peak in pressure when ignition occurs.
- Video recording at very high frame rates.

If the setup has optical access and depending on the diagnostics method used, this method can also allow for analysis of the different combustion processes occurring during ignition and general characterization of the reaction zone. Some of these optical diagnostic methods are:

- High speed video recording in combination with band pass filters to exclude or include certain wavelength ranges and highlight chemical processes.
- Emission and absorption spetroscopy (Raman spectrographs, IR spectrographs ...).
- High speed Schlieren movies and shadowgraphs.

The biggest disadvantage of the drop-test method is the fact that it does not allow for very good or reproduceable mixing of the components. The only kinetic energy added to the system is in the form of the drops velocity before impact. In a hypergolic rocket engine, however, the two components are typically injected and sprayed at high speeds. This means that the delay times measured with the drop-test method typically only represent a relative delay time characteristic to that setup and are not universal. A method to better understand the measured relative delay time is to establish a baseline by measuring the IDT of known conventional hypergolic fuels in the exact same setup with the same conditions. For these conventional fuels, the ignition behavior in actual engines is known.

The setup to perform drop tests can range from just a syringe and a bowl to an air-tight temperature and pressure regulated chamber with complex diagnostics instruments. A number of academic- and research institutions have made use of different implementations of this type of setup. A few of the more recent ones will be briefly presented here.

2.2.1 Existing Setups

The HYPERTESTER is a modular platform at Purdue University in West Lafayette, IN, used to perform hypergolic drop-on pool tests (see figure 2.3) [18]. It uses a piezo-electric diaphragm to sense the impact of the drop together with a photodiode that detects when ignition occurs. Additionally, a high speed video camera and a spectrometer/streak camera combination is used to analyze the reaction zone and allow for time-resolved spectroscopy. Data acquisition is manually triggered and a rod is used to manually actuate the syringe and create a drop. The cameras are automatically triggered by a laser-photodiode system when the drop interrupts the laser beam. The entire setup is contained within a box made up of alumninum profiles and windows. No pressurization or vacuum is possible.

The Center of Space Technologies in Warsaw has also made use of this methodology and constructed a pressure tight and closed combustion chamber to perform drop-tests (see figure 2.4) [19]. The chamber can withstand pressures of up to 40 bars and contains a heating element that allows to precisely control the temperature of the substance in the crucible. IDT evaluation is performed using a high speed video camera with the help of external LED light sources for illumination.

A joint effort between the Northwestern Polytechnical University and Jiatong University in Xi'an and the Chinese Academy of Engineering Physics has brought forward another drop-test setup that utilizes both a high-speed camera that captures the entire ignition and flame propagation as well as a long-focus microscope that allows for a much more detailed analysis of the fluiddynamic processes leading up to ignition [20, 21]. The droplet release height was adjustable and



FIGURE 2.3: The HYPERTESTER drop-test setup at Purdue University [18]



FIGURE 2.4: Drop-test setup at the Center of Space Technologies in Warsaw [19]

the experiments were performed at ambient conditions.

These are just a few of the already existing drop-test setups that show the different ways in which it can be implemented.

2.2.2 Setup for this Thesis

For this thesis, a setup is to be designed and constructed that makes use of high speed video recording to both determine the IDT as well as analyze the reaction processes in conventional and novel hypergolic ignition. Additionally, the light spectrum of the flame emission is to be analyzed using a spectroscope. The main goal is to increase the reproducibility of the IDT results as much as possible. To achieve this, as many of the factors that have an impact on the IDT as discussed in 2.1.2 should be kept constant or controllable. More detail on the specific requirements the setup has to meet and how they impact the chamber design are discussed at the beginning of the third chapter.

2.3 Optical Spectroscopy

Optical spectroscopy is the process of 'splitting up' an objects light into its component colors i.e. wavelengths. Dissecting and analyzing the resulting spectra can give information on a plethora of physical properties of the object. A prominent example is the use in astronomy, where the spectral analysis of the light coming from a celestial object can give information on the objects size, temperature or composition [22]. When this is done for the light produced by a flame, the process is commonly referred to as flame emission or combustion spectroscopy. To understand how a spectra reveals these types of information, one must understand the underlying atomic processes [23].

2.3.1 Atomic and Molecular Spectra

An atom consists of a core of protons and neutrons surrounded by a cloud of negatively charged electrons. Quantum mechanics dictate, that these electrons can only have discrete energy levels (also referred to as 'eigenvalues'). When an electron transitions from a excited state to a lower energy state, that difference in energy is mostly emitted as a photon. The energy of the emitted photon is directly proportional to its frequency or wavelength according to the fundamental Planck equation:

$$E_{Photon} = h \cdot \nu = h \cdot \frac{c'}{\lambda} \tag{2.1}$$

where ν is the frequency of the light, h is Planck's constant, c' is the speed of light and λ is the wavelength. Such an atomic transition results in a single discrete emission spectral line with finite width. Similarly, the process can be reversed: if an electron absorbs a photon with the correct energy, it can jump from its current state to a higher energy level, resulting in an absorption line. Every atom has many different possible electron transitions resulting in emission and absorption of different energy levels or wavelengths (according to eq. 2.1) making up a spectrum entirely unique to that atom. It is for this reason that through spectroscopy, the elements of the object can be identified. Figure 2.5 shows the Balmer series of the Bohr model for hydrogen showing the resulting wavelengths for different transitions to the ground state n = 2. Whilst the Bohr model correctly predicted the levels for hydrogen, it had some major shortcomings that were only resolved later on by the quantum mechanical model. It does, however, nicely demonstrate the general principle of discrete energy levels.

A molecule is formed by the chemical binding of two or more atoms. Its energy levels are also quantized, however in a much more complex manner than those of an atom. Rather than there just being different electron energy states, the energy structure is also made up of vibrational and rotational energy states, some of which depend on the temperature of the molecule. This results in a set of evenly spaced emissions lines, so called molecular bands, rather than just a single emission line as seen in atoms. An illustration of these different energy levels in an atom is shown in figure 2.6.

In reality, the emission lines are broadened by a number of different effects such as Doppler broadening, Lorentz broadening and Holtsmark broadening [23], none of which will be discussed any further here. As a result, emissions lines are actually peaks with a wider base that narrows





FIGURE 2.5: The Balmer series of the Bohr model for hydrogen including the resulting wavelengths for different transitions to the ground state n = 2 [25].

FIGURE 2.6: Illustration of a molecular energy level diagram with electronic, vibrational and rotational levels [23].

down towards the top.

2.3.2 Flame Emission Spectroscopy

In a flame or in combustion, the thermal energy created in the chemical reaction supplies the energy needed for higher energy states in the atoms and molecules involved in the process. When these subsequently return to their ground state, photons of both the visible as well as non-visible region are emitted. This effect is called chemiluminescence. As it is emitted from the flame itself, it can be measured without the need of any external excitation, as is the case with other methods of spectroscopy such as laser-induced fluorescence (LIF) spectroscopy [26]. A significant part of the radiation emitted in the UV and visible region of a flame is caused by short-lived intermediate species, so called radicals, that are typically denounced by a star (*) such as OH*, CH* and C₂*. The OH*-radical and the short-wave OH band it is a part of especially have been the subject of recent research in the field of combustion. Its visualization using high-speed cameras with a band pass filter has been used to make the flame reaction zone visible in hypergolic reactions between MMH and NTO [27] and LOX/H2 ignition (figure 2.7 [28]. Spectral analysis of the OH band (fig. 2.8) has been used to detect groups of emission lines who's intensities are a function of temperature [29, 30] and thus allow an nonintrusive way to determine the flame temperature. This was also performed to derive hydrogen flame temperatures in a research rocket combustor at the DLR [31].

In a similar way, alkali metals in flames have been analyzed spectroscopically and their ratios used to determine flame temperature, as alkali metals have very distinct emission lines [24, 32]. At the Fraunhofer Institute for Chemical Technology, emission spectroscopy was used to analyze the combustion flame of aluminum/copper oxide thermite [33].

Another type of spectroscopical flame analysis is absorption spectroscopy. Light of an external source is guided through the flame and its spectra measured. This spectra will show absorption lines, indicating the presence of certain atoms or molecules, much like emission lines.

These are just some of the ways that flame emission spectroscopy has been utilized. In general,



FIGURE 2.7: OH visualisation in a LOX/H2 spray



the identification of unknown peaks in the spectrum can yield information on the different molecules partaking in the chemical reaction, fuel-to-air ratios and flame temperature.

2.3.3 Czerny-Turner Spectrometer

A spectrometer is a device that divides up an incoming light signal into its different wavelengths. For this thesis, a triple grating Czerny-Turner spectrometer is used (a more detailed description of the used device will be given in chapter 4). Figure 2.9 shows the optical path in such a spectrometer. It is a dispersive spectrometer that uses a reflective diffraction grating to cause the dispersion effect.[34]



FIGURE 2.9: Top view drawing of the optical path in a Czerny-Turner Spectrometer [35]

The light signal enters the chamber through a slit and is reflected onto the diffraction grating by a collimating mirror. The resulting dispersed light is then focused onto the detector by another mirror.

Dispersion is the effect of the dependence of the refractive index on the wavelength of the light. This causes its spatial separation. The most prominent example of this effect is a rainbow, where water drops act as the dispersive medium. Angular dispersion is the correlation between the change in diffraction angle $\Delta\beta$ and the change in wavelength $\Delta\lambda$:

$$\frac{d\beta}{d\lambda} = \frac{m}{k \cdot \cos\beta} \tag{2.2}$$

k is the distance between grooves of the grating and m the order. In a spectrometer, however, the main interest is how far two wavelengths are spatially separated when the light reaches the detector. This is called linear dispersion and is the product of the focal length of the focusing mirror and the angular dispersion.

$$\frac{dL}{d\lambda} = f \cdot \frac{m}{k \cdot \cos\beta} \tag{2.3}$$

This means that a smaller distance k or a finer grating as well as a greater focal length result in a higher linear dispersion.

Another important property of a spectrometer is its spectral resolution. It is defined as

$$R = \lambda / \Delta \lambda \tag{2.4}$$

where λ is the central wavelength between two neighboring signals that can be safely determined and $\Delta \lambda$ is the distance between them. Two equally high signals are defined to be 'safely determined' when they are separated by a signal drop of at least 10% below the maximum. The width of the entrance slit, the fineness of the grating and the focal length of the focusing mirror all have an effect on R. Typically, the slit width and the grating can be changed. A smaller slit results in a higher spectral resolution but an overall loss of signal intensity. A finer grating results in a higher spectral resolution, however also in an increase in noise as well as a smaller total observable wavelength range.

Gratings are not equally efficient for all wavelengths, but rather are tuned to be efficient in certain regions depending on various factors such as the shape, angle and depth of the grooves. The wavelength for which the grating is most efficient is commonly referred to as the 'Blaze Wavelength' [36]. Figure 2.10 shows exemplary grating curves of a grating with 150 grooves per mm with different blaze wavelengths.



FIGURE 2.10: Grating curves for different blaze wavelengths [37]

3 Chamber Design

This chapter covers the design and construction of the reaction chamber itself. Starting off, the different requirements the setup needs to meet are discussed. The final design is then briefly presented, followed by a more detailed description of important design aspects and how they fulfill the aforementioned requirements.

3.1 Design Driving Requirements and Conditions

Before the design of the chamber can be tackled, the different requirements it needs to fulfill are identified. These requirements are derived from the scientific objectives the setup aims to fulfill as well as the theoretical background of its constituents.

- (R₁) Most importantly, the setup should minimize the fluctuation in or better yet make controllable as many pertinent variables as possible that might have an impact on the IDT. As discussed in 2.1.2, these factors can be of both physical and chemical nature. For the drop-test setup, this means that the chamber should be fully enclosed and the height and size of the droplets should be adjustable.
- (R_2) Static-wise the chamber should be able to withstand the peaks during ignition as well as pressures of 0.3 bar and lower. This in combination with an inlet for inert gas will allow to create an inert atmosphere inside the chamber. Furthermore, the impact of initial pressure on the ignition can be investigated.
- (R₃) Optical access for high speed cameras and spectroscopy down to the UV region (\sim 300 nm) is necessary. A minimum of two windows should be placed opposite of each other to allow for spectroscopic absorption measurements and recording of Schlieren.
- (R₄) If enclosed, there should be easy access for cleaning, exchanging of parts and so on.
- (R₅) The chamber should allow the performance of the tests from a distance to ensure safety.
- (R_6) The setup should be useable for a large variety of propellants and not just limited to a particular class. All parts that could come in contact with the tested substances need to be chemically resistant to them. This is especially critical for hydrogen peroxide and hydrazine.
- (R₇) Temperature and pressure measurement of the inside of the chamber to monitor conditions.
- (R_8) The entire chamber needs to be light and compact enough so that it can be moved in and out of a chemistry laboratory fume hood. This way, potentially harmful and toxic fumes that might result from combustion are carried away safely.
- (R_9) Cooling of the fuel or oxidizer if needed (especially for the volatile conventional fuels).

Just from these requirements alone, a first conceptual sketch of the chamber was made (fig. 3.1).

3.2 Design and Construction of the chamber

All of the before mentioned requirements impact the design of the chamber in one way or another. In this chapter, the design of the different parts of the chamber and how they fulfill the requirements are discussed. Rather than showing the finished design at the end of the section, it is shown here together with a short summarized description so that its different parts can be referred to. More important design aspects are then discussed in greater detail than smaller less



FIGURE 3.1: First conceptual sketch of the chamber design

important ones, since going into detail for each and every step would be excessive. The final design drawings can be found in the appendix.



FIGURE 3.2: Final chamber design

The chamber consists of a 216 mm long section of a 150 x 150 x 5 mm square aluminum profile with windows on three sides to allow optical access. Additionally, one side has a panel that can be removed entirely to allow physical access. On the back side there are connections for both water and a vacuum pump. The open ends of the profile are closed with two 150 x 150 x 10 mm aluminium plates. Placed on top of the chamber is a syringe pump that is used to inject the propellants into the chamber. The top plate also has connections for a pressure transducer, a barometer, a thermoelement and a pipe to feed in the inert gas.

3.2.1 Chemical Compatibility and Resistance

It was necessary to determine which materials were sufficiently chemically resistant against the used substances, the most critical being hydrogen peroxide and hydrazine. Materials of interest were some sort of aluminum alloy rather than stainless steel for the structure to reduce its weight and an elastomer for the sealing where necessary.

Chemical resistance of a material when used in HTP systems is typically divided up into four different classes [5, 38]. Class 1 materials are those that can unrestrictedly be used with HTP. Class 2 materials are those that can be safely used for repeated short-time contact with HTP. Materials of class 3 should only be used for short-time contact with HTP and class 4 materials are not recommended for use with HTP at all. For this setup, the materials used should be class 1 or 2. According to [5], 1000- and 5000-series aluminum alloys as well as some 6000-series aluminum alloys fall into either class 1 or 2. In general, the Al alloy should contain little to no copper. FKM/Viton [39] is categorized as class 2 and can be used for sealing for example in o-rings.

According to [40] the following aluminum alloys are compatible with hydrazine: 1100, 2014, 2024, 4043, 5052, 6061 and 6066. Viton is partially compatible and will suffice.

3.2.2 The Basic Chamber Design

Three possible concepts for the basic chamber structure were identified, each design having its own set of advantages and disadvantages.



FIGURE 3.3: Basic CAD models of the three proposed chamber designs

The first proposed design (figure 3.3a) is made up of off-the-shelf aluminum profiles (such as ITEM or Rexroth). This design allows for a relative simple assembly, good accessibility and a low weight. However, getting it air-tight is laborious. The optical access is good.

The second design (figure 3.3b) consists of a hollow square profile or square tube in which openings are milled out for the windows that are clamped down on to the side by metal frames. The biggest advantage of this design is that it provides good air tightness while still being relatively easy to access (for example with a door on a flat side). The downside of this design is its high weight and its rather complicated assembly. The optical access is more or less equal to that of the first design.

Finally, the third design (figure 3.3c) consists of a glass pipe clamped down between two surfaces. This design allows for great optical access and easily achievable air tightness. However, accessing the inside is only possible with considerable effort. Furthermore, a piece of glass of this size that fulfills the spectroscopical requirements is substantially more expensive than flat windows.

The design that was ultimately chosen was the second proposed design out of a hollow square tube. It is a compromise between design (A) and (B) allowing for good air-tightness and optical access while still granting physical access with relative ease. A desirable size would be a tube of 15 by 15 cm and a height of around 25 cm. Gathering information on readily available square tubes showed that the upper limit in thickness for a tube of dimensions 150 x 150 mm is 5 mm. Typically available tube materials are an AlMgSi0,5 alloy (EN-AW 6060), stainless steel and structural steel. Since the composition of Al 6060 is only slightly different from Al 6061 [41], which is known to be compatible with both hydrazine and HTP (see 3.2.1), and contains even less copper, it can be assumed to be sufficiently chemically compatible. Stainless steel is also compatible, however less desirable as it is heavier and more expensive.

Strength Calculation

To ensure safety and functionality, an estimate had to be made of the structural integrity of such a tube. In order to do so, one side of the tube was treated as a clamped metal plate with the dimensions 250 x 100 x 5 mm subjected to a uniformly distributed force resulting from a pressure differential Δp . The resulting deflection f at the plate center can be calculated with

$$f = \frac{cS_F \Delta p b^4}{E_m t^3} \tag{3.1}$$

where S_F is a safety factor, b is half of the shorter side of the rectangle, E_m is the E-module of the plate material, t is the thickness of the plate and c is an empirical constant depending on whether or not the plate is clamped and the ratio of the longer edge a to the shorter edge b [42]. The aforementioned Al 6060 has an E-module of 70000 N/mm² [43]. For a = 125 mm and b =75 mm, c = 0.413. Inserting into (3.1) gives a deflection of 0.6 mm for a plate thickness of 5 mm, a pressure difference of 2 bar and a safety factor of 2. Using stainless steel with a significantly higher E-module is thus not necessary. The tube that was ordered and used is a 150 x 150 x 5 mm Al EN AW 6060 square tube that was cut to the height of the chamber, approx. 22 cm.

Sealing of the Open Tube Ends

A wall thickness of just 5 mm brings along with it the problem, that the tube ends can not simply be closed off by drilling holes into the tube cross-section and screwing down a metal plate onto it. Using brackets from the outside is also not an option, since a force pushing down onto the cross section is needed if any type of seal is to be achieved. Instead, 30×30 mm square profiles are used as brackets attached to the inside of the chamber with nuts and bolts.



FIGURE 3.4: 3D model of sealing concept at the tube ends

The bolt threads through the chamber are sealed using teflon tape. Eight M6 grub screws are sunk into 7 mm deep blind holes and glued in place with LOCTITE on a 10 mm thick plate made of Al EN AW 6060 with dimensions 150 x 150 mm. The bolts are lined up with holes in the square profiles and then clamped down with nuts (see fig. 3.4). To create a seal, 1 mm thick SIGRAFLEX graphite sealing is cut to the dimensions of the tube cross-section and placed between the tube and the Al plate. When the nuts are tightened, the graphite is squeezed together and creates a seal. The chemical compatibility of the graphite seal is less critical, as it does not come in contact with any of the substances.

Removable Side Panel

For the sake of allowing easy access to the inside of the chamber, one side of the chamber is designed to be removable. To achieve this, a large opening as well as a 1 mm deep and 12 mm wide ledge surrounding it are milled onto one side. Four M6 grub screws, one in each corner, are screwed and glued into place. 1 mm thick graphite sealing is cut to fit snugly onto the ledge. The removable panel is cut out of the same 10 mm thick Al sheet as the end plates with the exact dimensions of the surrounding ledge and four holes are drilled into the corners of the panel so that they line up with the grub screws. Using winged nuts, the panel can be clamped down onto the graphite sealing ensuring that the door is air-tight.



FIGURE 3.5: 3D model showing the removable side panel

3.2.3 Window Material and Thickness

In order to allow for spectral analysis of the occurring combustion, the glass used for the windows should have a transmission of 90% or higher for wavelengths ranging from 300 to 800 nm. It should also be able to withstand the forces resulting from the pressure differential between the inside and outside of the chamber as well as have a small thermal expansion coefficient. Figure 3.6 illustrates the wavelength range for which different optical substrate materials are permeable for light.



FIGURE 3.6: Transmission wavelength range for different optical substrates [44]

UV-fused silica (also known as fused quartz) and sapphire are the most commonly used and thus typically cheapest glass types that fulfill the requirements. Because of its lower price and plenty of on-site experience in usage, quartz glass was chosen.

To calculate the required thickness, dimensions of 120 by 80 mm are initially assumed. A window of this size would give enough viewing area for both the high speed camera and the spectroscope while still comfortably fitting on the side of the chamber. To increase stability, the window is to be clamped down. According to [45], the thickness T of a clamped rectangular window is given by

$$T = L\sqrt{\frac{S_F K}{2}} \sqrt{\frac{\Delta P}{F_a (1+R^2)}}$$
(3.2)

where L is the length of the window, S_F is a safety factor, K is an empirical constant depending on the method of support, P is the load per unit area, F_a is the common apparent elastic limit of the window material and R is the ratio of length over width (L/W). Assuming a safety factor of 4 and a value of K = 0.75 for a clamped perimeter, this equation can be simplified to

$$T = 1.23\sqrt{\frac{\Delta P}{F_a(1+R^2)}}\tag{3.3}$$

For an apparent elastic limit of 60 GPa for quartz glass [46] and a pressure difference of 2 bar, which is a strong overestimation of the expected pressure peaks, this equation yields a required thickness of around 5.8 mm. During the process of getting quotes from different producers for three windows of roughly these dimensions, 4 leftover UV graded fused silica windows from a past project came into consideration because of their suitable dimensions. These windows have a dimension of 115 x 95 x 16 mm with rounded edges of 3 mm and were thus well suited for this application.

3.2.4 Mounting and Sealing of the Windows

An important design objective was the installation of the windows and getting them to be air tight. Past experience on-site has shown that installation of UV-fused quartz windows can be tricky as they can be easily damaged if not installed correctly. As a general rule, the glass itself should have no direct contact with any of the metal and the surface the window is placed upon should be even, as even the smallest irregularities could introduce localised stress when the screws are tightened that could cause the glass to shatter. The general concept behind the window mount is shown in figure 3.7.



FIGURE 3.7: Window mount concept

Essentially, the window is clamped down onto the surface of the chamber by a frame and screws. On the chamber side, a groove is milled around the entire window opening that holds an o-ring sealing cord on which the window rests. When the screws are tightened, the sealing cord is squeezed into the groove and forms an airtight seal (fig. 3.8). It is therefore of great importance, that the depth and width of the groove as well as the diameter of the o-chord are chosen in such a manner that a uniform seal along the entire outside of the window is formed while still maintaining a gap between the glass and the metal. On the frame side, rubber padding ensures that the window has no direct contact with the metal.



FIGURE 3.8: Cross section of the window clamped down onto the chamber side

For the seal, a cord with a diameter of 2.5 mm made from Viton/FKM was chosen. The groove was designed with the dimensions according to [47], with a change in depth from the

recommended 1.9 mm to just 1.75 mm to ensure that a gap of sufficient size remains between the glass and the structure. The cord was then cut to the right length, glued together with Loctite 406 glue, coated with vacuum fat and placed into the groove. For each window, a total of 16 M5 allen screws are used to clamp down the window. By using a higher quantity of smaller screws rather than a few bigger ones, the load on the glass is distributed more evenly. This design is implemented on three sides of the chamber, including the removable panel.

3.2.5 Drop System

A central design aspect of the chamber is the drop system. It determines the amount of fuel and oxidizer that react with each other as well as the dynamics of their collision and mixing. As discussed in 2.1.2, these factors can have a significant impact on the IDT and should remain constant.

The system consists of a syringe, a cannula and a watch glass dish. To create a reliable and constant drop size, medical cannulas are used. These are attached to a syringe. When the syringe is pushed down, it creates a drop at the tip of the cannula that falls off and onto the watch glass when reaching a certain size. Two cannulas and syringes are used to allow both the pre-dropping of the first component A, which will collect at the bottom of the dish, and the second component B, which is dropped onto the other (See concept sketch 3.1). The cannula dropping component A is placed slightly off-center whilst the cannula dropping component B is placed directly over the center of the dish. A difficulty lies in getting the cannulas into the sealed-off chamber while remaining air tight. To achieve this, the cannulas are epoxy glued into a female connector that can be screwed onto its male counterpart on the top of the chamber. This allows easy exchange of the cannula for both oxidizer and fuel. Cannulas with different diameters and lengths can be used to produce drops of different sizes and different impact speeds.



FIGURE 3.9: The final design of the syringe pump

Syringe Pump

In order to allow for the actual testing to occur from a safe distance and at consistent conditions, a syringe pump was designed that pushes the syringes. Originially, two different designs were considered, one using a hydraulic actuator and the other an electric. The pump should be able to move the syringe in both directions and hold them in place even when the chamber is put under vacuum. Figure 3.9 shows the final design.

The linear stepper motors used are 12,4 V unipolar 4 phase stepper motors with a maximum traverse of 10 mm. A single step length of 0.0167 mm should be small enough to precisely create single drops. More detail on the power supply and control is given in chapter z. The syringe can easily be replaced, thus allowing to test different substances or choose which component is pre-dropped. The pump is designed to hold 5 ml syringes with centered tips by Braun.

Combustion Vessel and Cleaning System

Another measure implemented to increase safety is an extinguishing and cleaning system. To achieve this, the dish is held by a metal bracket connected to a small motor which can rotate the dish. A water nozzle connected to a pipe with an electromagnetic valve is placed below the dish. After combustion, the dish can be turned upside down and sprayed down by the nozzle to remove residue and extinguish unwanted flames (see fig. 3.10).



FIGURE 3.10: Step-by-step illustration of the cleaning system



FIGURE 3.11: Close-up of the implemented system

4 Test Bench Setup and Calibration

This chapter will cover the entire experimental setup dubbed 'HYPErgolic Drop-Test SetUP' or 'HYPED UP' for short. Since the chamber is to be placed into a laboratory fume hood, no pre-existing test bench could be used for data acquisition and setup control. Instead, the entire setup had to be designed from scratch.

The setup can be divided into four subsystems, excluding the actual chamber itself: measurement and test controlling (A), high-speed recording (B), spectroscopy (C) and atmosphere regulation (D). Figure 4.1 shows the four subsystems and their relationship to each other and the chamber.



FIGURE 4.1: Conceptual illustration of the HYPED UP test bench and its different subsystems

In the following, the design, setup and calibration, if required, of each subsystem is discussed in detail.

4.1 Subsystem A: Measurement and Test Controlling

At the core of the measurement and test controlling subsystem sits a National Instruments CompactDAQ-9178. CompactDAQ is a modular data acquisition platform by National Instruments consisting of a chassis controller module that can hold up to 8 I/O modules and controls the data transfer between them and a PC via USB. Communication with the controller and modules is achieved with the PC software LabVIEW, also built by NI. A wide range of modules with different functionalities exist, such as voltage measurement, digital I/O signal creation, current measurement and so on. For this setup, three modules are used. [48]

The first module is the NI 9472. It provides 8 digital output channels and requires an external power supply V_{sup} in the range of 6 - 30 V DC and a ground connection. Each digital out pin can independently set to be HIGH ($\approx V_{sup}$) or LOW (0 V) with LabVIEW. Each channel has

an LED indicator light that lights up when the channel is HIGH. The continuous output current per channel has a maximum of 0.75 A.

The second module used is the NI 9219. It provides 4 channels of 6 pins each for a variety of measurement types and does not require any external power supply. Some of the possible measurement types are voltage, current and resistance. Depending on the measuring mode used, the pins are wired differently. In this case, a channel is used to measure the voltage coming from the pressure transducer. The maximum voltage it can measure is 20 V.

The third module used is the NI 9214. It provides 16 channels to measure small voltages. With information on the thermocouple type, LabVIEW can then transform the measured voltage into the temperature in Celsius.

4.1.1 Syringe Pump and Cleaning System

The syringe pump utilizes two 4 phase unipolar linear stepper motors to move the syringes. Figure 4.2 shows a wiring diagram of such a motor.



FIGURE 4.2: Conceptual wiring diagram of 4 phase unipolar stepper motor

FIGURE 4.3: SAMOtronic stepper motor conroller overview

In order to rotate the motor, four of the six connections need to be grounded in the right order $(Q_1 \text{ to } Q_4 \text{ in fig. 4.2})$. The remaining two are connected to the power supply (+ V). While this could be done by manually implementing the sequence in LabVIEW and connecting the wires to the NI 9472 module pins accordingly, the 8 available output channels on the module would not suffice to individually control both motors. Instead, two SAMOtronic-uni stepper motor controllers by SAIA-Burgess Electronics are used. In its easiest configuration, this controller only requires a power supply to run the motor. The frequency of the motor can then be set by turning a knob on the controller. The controller has 5 additional digital inputs that can switch the motor on and off, switch between half- and full-step mode, change the turning direction (or in this case, if the shaft is moving in or out), change the frequency of the steps and shut off the internal frequency generator. Three flip switches on the controller allow to choose between the different modes that make use of these inputs. An incoming TTL-signal is considered HIGH if it is between 2 and 5 V and LOW for values smaller than 0.8 V.

For this setup, a variable motor speed (frequency), the option of changing the turning direction (CW/CCW) and the possibility of switching the motor on or off are required. The three corresponding inputs on the controller (2,4 and 5) are wired up with three digital outputs on the NI 9472. The NI 9472 is connected to a 5 V power supply, as this is the maximum voltage the stepper motor controller digital in- and outputs can take. The six connections coming from the
stepper motor are connected to the corresponding pins on the controller. The controller itself is wired up to a 12 V DC power supply. This is where the energy required for the stepper motors stems from. During testing, it was discovered that when switching from HIGH to LOW on any of the NI 9472 outputs, the voltage fails to drop below the threshold of 0.8 V needed for the controller to register the signal as LOW. To prevent that, the lines were gapped to ground with a pull-down resistor of 1 $k\Omega$. This allows a high enough current to flow and the voltage to drop sufficiently low. The same is done for a second motor and controller. Stepper motor number 2 is connected to outputs 4, 5 and 6 on the NI 9472.

The cleaning system requires a motor to turn the dish as well as an electromagnetic valve that can be closed and opened electronically. Both of these things can also be achieved using the NI 9472 digital output module. The motor used is a small electronic motor geared down to a very low RPM of around 50. It is a 6 V motor and thus runs well enough with the 5 V the NI 9472 is limited to due to the SAMOtronic controller. The positive wire of the motor can be directly connected to one of the 2 free pins on the module (number 3). The negative end is connected to ground. The electromagnetic valve requires a voltage of 12 V and can thus not be connected directly to the NI 9472. The power supply used to power the SAMOtronic controller, however, is at 12 V. As a workaround, a 5 V relais was purchased and connected to the remaining NI 9472 output (number 7). When the relais is powered on by the NI 9472, it closes the 12 V circuit of the solenoid valve and the valve opens up.

The electric circuit of the syringe pump and cleaning system in its entirety is displayed in 4.4.



FIGURE 4.4: Wiring diagram of the syringe pump and cleaning system

To increase safety and compactibility as well as to protect the sensitive electronics, the two motor controllers and the servo are placed into an enclosed box. Two manual flick switches are installed on the outside of the box to cut the power to the controllers and thus the syringe pump as an additional safety feature.

4.1.2 Temperature and Pressure Measurement

Temperature

To measure the temperature in the chamber, a K-type thermocouple is used. A thermocouple is a common and easy to use temperature sensor that does not need an external power supply to function. It makes use of the Seebeck effect, one of three known thermoelectric effects, to measure a voltage resulting from a temperature gradient and a consequential electromotive force (emf) along a electrically conducting material. In a thermocouple, two different materials are joined at a junction. The physical properties of the materials and the type of junction impact the temperature range that can be measured, as well as the response time and the resulting error in the measured values. In a K-type thermocouple, the two materials used are nickel-10% chromium (+) and nickel-5% aluminum and silicon (-). It is often referred to as the general purpose thermocouple as it is low in price and serves most purposes.

For this setup, a class 1 K-type thermocouple with a probe sheath diameter of 0.5 mm and a length of 100 mm is used. The sheath, which is the cover material surrounding the actual thermocouple wire, also effects the range of temperature the thermocouple covers and in this case is made of stainless steel. The resulting measuring range is from -200 to 800 °C. According to DIN EN 60584, the allowed limit of error for temperatures between -40 and 1000 °C is 1,5 °C. A probe diameter of 0.5 mm was chosen, as a smaller diameter typically reduces the response time. The thermocouple is screwed onto an adapter on the surface of the chamber that clamps down on the wire when tightened and thus creates a seal. [49]

The two wires coming from the thermocouple are connected to a positive (TC0+) and a negative (TC0-) thermocouple connection respectively on the NI 9214. As it does not require any power supply, no further wiring is required.

Pressure

Apart from the barometer that analogically displays the pressure in the chamber and allows for a quick rough estimate of its current value, the pressure is also recorded digitally using a piezoresistive strain gauge pressure transducer. A strain gauge pressure sensor makes use of the piezoresistive effect, where a deformation of a conductive material, in this case a deformation caused by a pressure difference, causes a change in electrical resistance of said material. That change is detected as a change in voltage of a Wheatstone bridge and further amplified. A polynom relating that voltage to a pressure that is determined through calibration is then used to get the final value.

The sensor used is a PR3102 Protran standard industrial pressure transmitter by Althen with a measuring range of 0 to 10 bar and an output signal from 0 to 5 V. The main reason it was chosen is that it does not require a constant power supply voltage but rather accepts voltages in the range of 13 - 30 V DC. This allows to keep the number of required power supply units of the setup to a minimum as the 12 V DC supply for the stepper motor controller and EM-valve can be used. The down side of such a sensor is that it tends to be less precise. The calibrating polynom is a quadratic function of the form

$$p = A_0 + A_1 * V + A_2 * V^2 \tag{4.1}$$

where V is the measured voltage in mV, p is the resulting pressure in bar and A_i are coefficients given in the following table:

coeff.	value	unit
A_0	$-1.04102\cdot 10^{-2}$	bar
A_1	$1.99826 \cdot 10^{-3}$	$\mathrm{bar/mV}$
A_2	$-3.30549 \cdot 10^{-10}$	$\mathrm{bar/mV^2}$

TABLE 4.1: Calibrated coefficients of the pressure transducer

The coefficients were determined in the calibration laboratory on-site. Four of the six available pins on the electric plug of the PR3102 are used, 2 for the power supply (A and D) and two for the signal (B and C). The two signal carrying wires are connected to pins 4 and 5 on the NI 9219.



FIGURE 4.5: Wiring diagram of the PR3102 pressure transducer

The open end of the pressure transducer has a M14 x 1.5 thread around it and is screwed onto the top of the chamber with a U seal ring in-between.

4.1.3 LabVIEW Routine and User Interface

The communication with the cDAQ and the modules is done via LabVIEW. LabVIEW is an environment for a visual programming language named 'G'. It is especially well-suited for dataacquisition and instrument control. A routine or 'virtual instrument' in LabVIEW consists of a back and a front panel. The front panel is where the user interacts with the instruments using controls (inputs) and indicators (outputs). The back panel or block diagram is where the actual visual programming takes place and the controls and indicators appear as terminals. Different structures and functions can be used to determine what to perform with the incoming controls and what data is passed on to the indicators. Figure 4.6 shows the final HYPED UP LabVIEW front panel.

It is divided into different sections for the different components that are controlled. At the bottom of the screen, the current pressure and temperature is graphically displayed. Above that, the recording of the pressure and temperature data can be turned on or off. The file path for where the data is to be saved can be either entered manually or chosen on-screen. In the top left, the two motors are controlled. A click of the ON button activates the motor for the time period entered into the box below. The frequency and subsequentially speed of the motor is set by entering a value in hertz. A progress bar and a numeric value show how much of the set ON-time has elapsed when the motor is turned on. Finally, a flick switch dictates whether the motor moves inward or outwards. In the section 'cleaning', the solenoid valve can be opened and closed and the bowl turned for a defined time.

4.2 Subsystem B: High Speed Recording

High-speed video recording to determine the drop impact and IDT is performed using a Photron FASTCAM SA5 as well as a SA-X2. The SA5 is a monochromatic camera that records at a maximum resolution of 1024 x 1024 pixels and with up to 7000 frames per second. The smaller the resolution is chosen to be, the higher the maximum fps. The SA-X2 is a color camera with an equal maximum resolution at a frame rate of 12500 fps [50]. Both cameras connect to a laptop (PC 2) via ethernet and are controlled using the Photron FASTCAM viewer software version 3.50. A 1.5 W LED attached to the camera is used to sufficiently illuminate the chamber interior, as filming at a higher frame rate drastically reduces the brightness. Furthermore, the aperture of the camera is closed slightly to increase the depth of field and thus ensure that the drop impact is in focus, which further reduces the brightness of the image. A lens with a focal



FIGURE 4.6: A screenshot of the HYPED UP LabVIEW front panel

length of 100 mm is used, allowing the camera to be placed outside of the hood on a tripod. In order to properly see the surface of the liquid at the bottom of the dish, the camera is placed at an angle looking through the front window. At a frame rate of 3600 fps and an exposure time of 1/3600 s, the image is found to still be sufficiently bright while providing a high enough temporal resolution (one image roughly every 0.28 ms) for our purposes.

Using the PFV software, a trigger signal can be created when a change occurs in the viewing field of the camera. To do so, an area as well as a threshold is defined, that tells the software by how much percent the average of the image bin entries in said area should stray from the pre-determined background before the recording is triggered. This trigger signal is then passed on to the spectroscope via a BNC cable. This is used to auto-trigger both the camera and the spectroscope when the drop falls into frame, ensuring that the ignition is captured. More on the spectroscope-triggering is discussed in the following chapter.

4.3 Subsystem C: Spectroscopy

The spectroscopy subsystem itself is made up of different components as shown in figure 4.7.



FIGURE 4.7: Schematic of the components of the spectroscopy subsystem

The spectroscope used is the SpectraPro2756 in combination with the PI-Max 2 intensified CCD (ICCD) camera and the ST133 controller, all by Princeton Instruments. The SP2756 is a Czerny-Turner Spectrometer with a focal length of 750 mm and an aspect ratio of f/9.7. It has an interchangeable triple grating turret for three gratings of the size 68mm x 68mm with different groove densities and a blazed wavelength for which it is most efficient. As per equation 2.2, this results in different values of linear dispersion and spectral range. The following gratings are used:

grating [g/mm]	blazed wavelength [nm]	linear dispersion $[nm/mm]$	sp. range [mm]
150	500	8.8	235
600	500	2.16	57
1800	500	0.64	17

TABLE 4.2: Gratings of the spectrometer and the resulting linear dispersion and coverage [37]

The given linear dispersion and spectral coverage is for a focal plane of 26.8 mm. The SP2756 is configured with a side entrance slit for the incoming light and a front flange port where the split up light exits and the CCD camera is attached (fig. 4.8).

The slit width can be manually adjusted from $10 \ \mu m$ to $3 \ mm$. The light signal coming from the flame emission is passed on out of the fume hood to the spectroscope via a waveguide that is fixed to the spectroscope in a way that ensures the light passes the slit.

The PI-Max 2 system consists of a CCD sensor and an image intensifier housed inside the camera head as well as the ST 133 controller. The CCD sensor is the CCD30-11 front-illuminated open electrode high performance CCD sensor by e2v technologies. It has a size of 1024 by 256 pixels with a square pixel size of 26 µm, resulting in a total area of 26.6 x 6.7 mm. It is oriented in a way that the resulting spectral lines are parallel to the shorter side of the sensor. Its spectral range is from 200 to 1060 nm and it is specifically made for near UV spectroscopy applications. Its efficiency for different wavelengths, also called the quantum-efficiency when speaking of CCD sensors, is displayed in figure 4.9 [51].

The image intensifier is a HQf Gen III filmless intensifier [52, 53] that is fiber-optically coupled to the CCD array. It is a proximity-focused microchannel plate (MCP) image intensifier. Its



FIGURE 4.8: SP2750 configuration

width of 18 mm limits the total active surface area of the CCD intensifier combination to 18.0 x 6.7 mm. As the name indicates, the intensifier can be used to intensify the incoming light signal before it is read out by the CCD to the controller. This is especially useful for ultra low-light applications, such as spectroscopy, where some emissions lines might be extremely weak and hard to identify without further amplification. Additionally, it can be used to 'gate' the signal acting like a shutter. Only if the intensifier is biased 'ON' will it allow light to pass. This can be used to achieve ultra short measurements down to 2 ns. The intensifier is also not equally efficient for all wavelengths, as seen in figure 4.9. The combined efficiency of the CCD and the intensifier can be calculated simply by multiplying the efficiencies and is also included in figure 4.9.



FIGURE 4.9: Efficiency curves of the CCD and Intensifier as well as the combined curve

The camera head also houses a cooling system consisting of a multi-stage peltier element and a cooling fan. Keeping the detector temperature low increases the signal to noise ratio by reducing the dark current. Dark current is the result of spontaneously generated electrons and is a thermal effect.

The ST133 controller provides the high voltages required for the intensifier and controls the exposure timing, scan control and temperature of the ICCD.

4.3.1 Software for System Configuration and Data Acquisition

The configuration as well as data acquisition of subsystem C is controlled using the WinSpec/32 software on PC 3 via a USB connection to the SpectraPro. A brief overview of the main settings of the program is given here.

In general, the ICCD camera can be run in three modes: safe mode, shutter mode and gate mode. In safe mode, the high voltages in the intensifier are disabled entirely. This prevents that the intensifier or CCD array is accidentally damaged through high intensity light and resulting overexposure. In shutter mode, the intensifier is only biased 'ON' and passes light to the CCD for the chosen duration of exposure. During readout of the array it is biased 'OFF'. Finally, in gate mode the intensifier is gated on and off by the ST133 as if it were a mechanical shutter. For the HYPED UP, only the shutter mode is used as an additional controller module would be needed to perform an externally triggered measurement in gate mode.

The incoming data from the CCD camera are arrays of the dimension 1024 x 256 where each entry represents one pixel and with values corresponding to the intensity of the light. The data is displayed on screen as an intensity over x-pixel plot, where the values along the 256 y-pixels are averaged for each x-pixel to give the intensity at that pixel. Figure 4.10 shows an example using lines recorded of the fluorescent tube lamps on the lab ceiling.



FIGURE 4.10: From the raw CCD image to the intensity plot

The exposure setting controls the integration time on the CCD chip. The higher the exposure is chosen to be, the more light is collected on the chip. This can make the signal more visible, however it also increases the noise. The number of accumulations dictates how many measurements of the set exposure time should be added onto one another before saving the spectra. The number of spectra controls the amount of spectra that are recorded. For example, a number of accumulations of 5 and a number of spectra of 3 would result in 3 spectra that are each made up of the sum of 5 CCD readouts with the chosen exposure time. That makes a total of 15 cycles. Those three spectra would then be saved in the same file. The intensifier is used by setting a value between 0 and 255 for the gain, where 0 means no intensifying and 255 is maximum intensification of the light. A relationship between the gain and the measured intensities was determined and is discussed in chapter v.

Two timing modes are available in shutter mode: free run and external sync mode. In free run mode, one cycle follows the other as fast as possible until the user set amount of accumulations and/or numbers of spectra has been recorded. In external sync mode, a new cycle is started every time a TTL signal pulse reaches the Ext. Sync input on the ST133.

The only two things that are controlled in the spectrograph itself are the central wavelength of the current grating, that is which wavelength is at the center of the CCD, and which grating is being used. Both of these things are done by turning the turret using a stepper motor. After calibrating the gratings (see next section) the center wavelength and desired grating simply has to be chosen and the turret will turn to ensure just the right incident angle on the correct grating.

The recorded spectra are saved as .SPE files, but can be converted into ASCII txt-files directly in the WinSpec software.

4.3.2 Wavelength or X-axis Calibration

Before any measurements are made, the spectrograph needs to be calibrated. That is, a relationship between the x-pixel on the CCD and the wavelength of the light needs to be established.



FIGURE 4.11: The acquired spectra of the Hg(Ar) calibration lamp for two different gratings with peak locations

This is done using a light source that has distinct emission lines with known wavelengths. In this case, a Mercury Argon pen-ray line source by LOT-QuantumDesign is used. This lamp produces narrow and intense emission lines that are well documented and is specifically made for wavelength calibration of spectrometers and monochromators. The lamp is placed in front of the slit of the spectrometer and the calibration procedure is performed for all three gratings. The calibration procedure consists of three steps performed in the WinSpec/32 software. Simplified, the correlation between the x-pixel and the wavelength can be thought of as a linear one with the equation y = mx + b. First, the offset 'b' is determined. To do this, the grating is moved to the zero order peak (which is all the light). After manually choosing that peak on screen, the scale is then auto-adjusted so that the peak is exactly at the center of the CCD and at a wavelength of 0 nm. Next, the slope 'm' has to be determined. This is done using the peaks of the Hg(Ar)-lamp. The reference wavelength of a peak is entered and the corresponding peak chosen on screen. The software then automatically calculates the slope. Finally, the effect of dispersion has to be taken into account so that peaks on the far left or right of the window are also correctly calibrated. In order to achieve this, the grating is turned so that different peaks of the calibration lamp are first on the far left and then on the far right of the display. Together with the information on the reference wavelength of those peaks, the software then determines the best values through an iterative process. [54]

Figure 4.11 shows two of the acquired spectra of the calibration lamp. The third can be found in Appendix. It immediately stands out how the emission lines obtained with the finer grating (B) are much narrower than those in (A) due to the greater linear dispersion and better spectral resolution of the grating. This also increases the accuracy in determination of the peak wavelengths (more on that in chapter 5). Comparing the obtained peak locations with standard emission line wavelengths of Mercury from literature taken from the pen lamp datasheet [55] shows how the accuracy increases for finer gratings (see tab. 4.3).

Literature [55]	$150 \ \mathrm{GRT}$	600 GRT	1800 GRT
365.0	364.4	364.7	365.0
404.7	404.0	404.5	404.6
435.8	435.2	435.6	435.8
546.1	545.6	545.9	546.0
577.0	576.4	576.7	576.9
579.0	578.4	578.8	579.0

TABLE 4.3: Emission lines from literature and the measured lines using the three available gratings

4.3.3 Optical Fiber Alignment and Focus

As seen in fig. 4.7, the light coming from the flame is propagated to the slit entrance of the spectroscope using a waveguide or optical fiber. In order to capture the biggest possible amount of light, a biconvex lens as part of an optical collimator is used to focus the light from the flame onto the fiber entrance (fig. 4.12). To achieve this, the chamber is placed onto a Newport RPR Reliance optical table top with M6 mounting holes. A 30 x 30 mm cage with 10 cm long construction rods is screwed onto the table in front of the UV window that holds the lens and allows it to move along the rods. A fiber mounting adapter is placed at the end of the rods where the fiber is screwed on. To adjust the focus, a LED light source is attached to the other end of the fiber. The lens and cage are positioned in such a way, that a light spot of about 3 cm diameter is above the dish in the chamber where the flame is expected to be. Since light is unidirectional and linear, this ensures that the flame light inside that 3 cm diameter will be focused onto the fiber.



FIGURE 4.12: Optical collimator setup

4.3.4 Device Curve Determination

Every component that the light interacts with on its path from the flame to the CCD sensor has its own transmission, reflectance or efficiency curve that varies depending on the wavelength of the light. This leads to the measured spectra being distorted and not an accurate representation of the real occurrence. Rather than determining the aforementioned dependencies for each and every component, a curve for the entire setup is determined. This is done by using a light source with a continuous spectrum covering a wide spectral range whos exact intensity output is known. The light coming from that light source is then subjected to the exact same optical path as the light from the flame and its intensity is measured. By relating the known 'real' spectrum with the spectrum measured by the setup, a correction factor can be determined for every wavelength with which the measured data has to be multiplied with. The resulting curve is also know as the device curve. It is important that this step is done only after the wavelength has been calibrated. Essentially, this is the 'intensity' calibration of the setup.

The light source used is a tungsten halogen lamp. It is placed at the same position where the flame will be and turned on. To increase the accuracy of the measurement, only the intensity value of the central wavelength is used. Starting at a center wavelength of 250 nm, 10 spectra are recorded in steps of 3 nm all the way up to 850 nm. The exposure and gain is chosen in a way that no pixel is overexposed at any point and kept constant throughout the entire series. This procedure is repeated for all three gratings, as each grating has a different reflectance curve. For each central wavelength, the average of the 10 measured spectra is determined. The resulting spectrum is then normed to one in order to make it comparable. This yields the three curves displayed in fig. 4.13a. To get the correction factor, the measured curve is interpolated at the same wavelengths as the W-lamp data. Dividing the real intensity with the measured intensity for each wavelength respectively gives the correction factor at that wavelength. This yields three 'device curves', one for each grating (fig. 4.13b).

4.3.5 Gain Correction

As mentioned in 4.3.1, the intensifier is controlled through a gain value that is set to be anywhere between 0 and 255. In an attempt to quantify the effect of the gain on the measured intensity, one specific emission line of the Hg(Ar)-lamp was recorded for gain values from 0 up to 210 and its intensity determined. Plotting the intensity as a function of the gain reveals an exponential



(b) The resulting device curves for each grating

FIGURE 4.13: Device curve determination

correlation between the two. The intensity value at a gain of zero is normed to be 1 and an exponential fit of the form

$$f(x) = a \cdot e^{b \cdot x} \tag{4.2}$$

is performed (fig. 4.14).

The resulting fit equation represents a correction factor CF_{gain} with which the measured Intensity has to be multiplied with depending on the gain value that is chosen.

$$CF_{qain} = 0.6809 \cdot e^{0.02751 \cdot x} \tag{4.3}$$

This is a correction for the gain-intensity correlation of the ICCD. However, this does not allow for accurate intensity comparisons and is more of a way to visually present the rough order of magnitude in intensity difference. Reliable comparisons of intensity/peak height should only be made if the spectra were recorded with identical exposure and gain settings using the same grating.

4.3.6 Trigger Handling

As mentioned in chapter 4.2, a TTL trigger signal coming from the FASTCAM high-speed camera when the drop falls into frame is used to trigger the spectroscope. To achieve this, a



FIGURE 4.14: The determined intensity values for different gains as well as the exponential fit

BNC cable is connected to the TTL SIGNAL OUT cable of the camera and to the EXT SYNC female BNC connector on the back-plane of the ST133 controller. When the SP2756 is run in external sync mode, each incoming TTL signal triggers a new cycle. The camera only gives of a single signal at the start of the recording. However, to record multiple ignitions or possibly resolve one ignition event over multiple spectra, a continuous recording of spectra once the trigger is set is desired. This is accomplished using a pulse generator that is triggered by the incoming signal from the camera and monitored by an oscilloscope. The pulse width or frequency set on the pulse generator then determines the frequency in which spectra are recorded, assuming that the exposure time times the number of accumulations plus the readout time of the PI-MAX set in Winspec is smaller than the pulse width. Figure 4.15 shows the timing diagram and trigger chain of the setup.



FIGURE 4.15: Timing diagram for continuous spectra recording using a pulse generator

4.4 Subsystem D: Atmosphere Regulation

The fourth subsystem is not nearly as elaborate as the other three and consists of a vacuum pump and some source of inert gas. The vacuum pump is placed on the floor outside of the hood and both its inlet and outlet are connected to a hose respectively. The hose coming from the inlet is attached to the hose connector on the chamber. The the hose connected to the outlet is guided into the fume hood so that any potentially harmful gases sucked from the chamber are not released into the atmosphere. The bottle containing the inert gas is place outside of the vent and secured in place with a strap. A hose is connected to the bottle and the chamber. Both hose connectors on the chamber include a ball valve with which the connector can be opened or closed shut. This subsystem allows to lower the pressure inside the chamber and flush it with an inert gas if needed.

4.5 Further Preliminary Setup Investigations

Before drop tests were carried out with hypergolic substances, additional investigations were performed to ensure the correct functionality of the setup.

The dropping mechanism including the syringe pump and the camera triggering was elaborately tested with water. This included finding the correct settings for the trigger at the actual test lighting conditions. Furthermore, the constancy in the drop diameter created by the canula was ensured. It was also verified that the drop impact point was at the center of the liquid pool in the dish, so that the best possible mixing of the components is achieved. A number of vacuum tests were performed to check that the chamber was air-tight for pressures down to 0.4 bar and drop-tests were successfully performed with water under these conditions.

4.6 HYPED UP Test Bench and Setup Procedure

As the HYPED UP test bench is rather elaborate and consists of multiple subsystems, a clearly defined step-by-step setup manual is necessary to allow for a reliable and especially safe test procedure. Figure 4.16 shows a 3D model roughly showing the main subsystems and their orientation and placement with respect to each other and the fume hood in the laboratory.



FIGURE 4.16: The HYPEDUP test bench

The chamber and the electronics are placed inside the hood separated by a protective glass. The spectroscope is placed on a table outside of the hood and the camera is placed on a tripod in front of the hood. All three laptops are placed on the table, too. Figure 4.17 shows a picture of the assembled chamber inside the fume hood.



FIGURE 4.17: Image of the test chamber inside the fume hood

5 Experimental Procedure and Data analysis

This chapter discusses the steps involved in the experimental procedure of the HYPED UP. It then covers the process of how the raw data coming from the subsystems is processed and the data and its uncertainties are obtained.

5.1 Experimental Procedure

Once all the subsystems are up and running, the actual experimental procedure can begin. As potentially harmful substances are used, personal protective equipment such as a lab coat, protection goggles and gloves are mandatory at all times.

Preperation and Fueling

Depending on the drop height and size that are to be achieved, two canulas epoxy glued into a female screw connector are screwed into place on top of the chamber. A watch glass bowl is placed into the turning mechanism bracket. Two 5 ml syringes are then filled up to around the 1 ml mark with the oxidizer and fuel that is to be tested. First, the syringe containing substance B that is to be dropped is fixed into place on the syringe pump. A bowl of water is placed on the watch glass and the linear stepper motor B is slowly moved outwards until drops start forming at the canula tip. The duration set in LabVIEW is typically 15 seconds at a motor frequency of 20 Hz, but can vary depending on the viscosity of the fluid and how full the syringe is. Then, the second syringe containing the component that is pre-dropped (component A) is fixed into place. The conductor should ensure that the video image is correctly alligned and in focus and that the image trigger is set.

Testing

Stepper motor A is slowly moved until the desired amount of drops of component A have collected at the bottom of the dish (typically a motor frequency of 5 Hz is set). Pressure and temperature data acquisition is turned on. Then, stepper motor B is gradually actuated until a drop starts forming and eventually falls of. Typically, multiple drops of component B are dropped to allow for multiple ignition spectra to be recorded. After ignition has occured, the dish is turned and the solenoid valve opened to clean the dish and extinguish any residual chemical reactions. The video recorded of the first drop test after refueling should be used to verify that the drop impacts the liquid at the center. If this is not the case, the canula and dish position can be adjusted accordingly. After saving the acquired spectra and videos and making adjustments in their settings if necessary, the procedure is repeated.

Refueling or Shutting Down

Once either of the two components is used up, a bowl of water is placed underneath the canulas. Both or just one of the motors are then fully retracted and the syringes removed. The canulas are flushed with distilled water to remove any residue. If a different combination is to be tested, new syringes are used.

5.2 Spectral Data Analysis

Similar to an astronomical observation, the raw data recorded with the PI-MAX in itself is skewed by various effects, including the ones discussed in section 4, and needs to be corrected in a number of steps. Due to the large amounts of data produced in every measurement, this process is automated through a Matlab routine. To showcase these steps, an exemplary data taken with the 150 g/mm grating is used (Figure 5.1).

A typical spectral measurement of the HYPED UP consists of a number of spectra n all stored in an array as a ASCII file. The following table shows the structure of such a file.

x-pixel	1	2	3		1024
Wavelength	λ_1	λ_1	λ_1	•••	λ_{1024}
$Spectrum_1$	$I_{1_{1}}$	$I_{1_{2}}$	$I_{1_{3}}$	•••	$I_{1_{1024}}$
$Spectrum_2$	$I_{2_{1}}$	$I_{2_{2}}$	$I_{2_{3}}$	•••	$I_{2_{1024}}$
:					:
$\operatorname{Spectrum}_n$	I_{n_1}	I_{n_2}	I_{n_3}	•••	$I_{n_{1024}}$

TABLE 5.1: The structure of a typical obtained spectral data

Background Correction

Only some of the spectra contain actual measurements of the flame emission, as the recording is triggered before impact and continues to run for a number of spectra n set by the user. The remaining spectra can be used to determine the background. The first step is to identify which spectra contain background data and which flame measurements (or 'light' measurements) and to make sure none of the spectra are overexposed.

This is done by calculating the standard deviation (SD) of each spectra in the file. The minimum value of all the SDs is used as a baseline. Any spectra that has a SD greater than 2 times the minimum SD is defined to be a flame measurement, anything below is background. Additionally, any measured spectra that contains a value of 65535 is ignored, as this number represents the maximum value of a 16-bit binary number and indicates that the CCD sensor was overexposed. Sometimes, artifacts created for example by cosmic ray particles hitting the CCD sensor can appear, creating a drastic sharp peak. To prevent these from accidentally being categorized as a light measurement, each light spectra is shown on screen and the user decides whether or not to include the spectrum. An average of all light as well as background measurements is then calculated (Figure 5.1b and 5.1a). Subtracting the background from the light measurement yields a background corrected spectrum (Figure 5.1c). We have now reduced the array of multiple spectra to a simple x-y-plot.

Blind Spots Correction

As discussed in chapter 4.3, the intensifier reduces the area of the CCD onto which the dispersed light actually falls and creates 'blind' spots on the CCD and in the spectrum. These areas are removed as part of the routine (see figure 5.1d).



FIGURE 5.1: Plots showcasing the different data processing steps

Gain and Device Curve Correction

Next, the grating specific device curve is interpolated at the relevant wavelengths of the measured spectra and the correction factor applied to the data (see ch. 4.3.4). Figure 5.1e shows the interpolated correction factors and figure 5.1f the resulting corrected spectrum. In this step, the gain correction as discussed in 4.3.5 is also applied if a comparison between spectra is desired.

Baseline Correction

Finally, using a MatLab function called backkor.m written by Mazet et. al [56], a spectral baseline can be established and subtracted from the data. This serves the purpose of making discrete peaks more clearly visible by subtracting the underlying continuous spectrum. Of course, this way, any information on the intensity of the peaks is lost as each wavelength is corrected with a different value.

The function performs the estimation of the baseline by minimizing a non-quadratic cost function. The user can choose between different functions and orders that are displayed in a UI in order to evaluate which fit works best for the given data. Figure 5.1g shows the spectra normed to 1 as well as the determined baseline using an asymptric truncated quadratic fit. Subtracting that baseline from the spectrum yields the spectrum in figure 5.1h.

Comparing figure 5.1a and 5.1g impressively shows the importance of the different data correction steps, as the difference between the spectra is drastic.

5.2.1 Summing Up and Stitching Together Spectra

Since every grating has a limited spectral range, recorded spectra need to be 'stitched' together if a wider wavelength range is to be shown. This is implemented in a MatLAB routine. The requirement for this is that the spectra are recorded with the same grating and have some overlap in wavelength.

To achieve this, the routine reads in the already corrected but non-normed and non-baseline reduced spectra that are to be connected (fig.5.1g). Starting with the first file, the intensity and wavelength of the last entry are determined. In the next file, the entry that is closest to that wavelength but slightly higher is searched for. The difference between the intensity of that entry and the entry in the first file is defined as an offset. The entire second file is then shifted by that offset so that the intensity values at the end of the first and the beginning of the second file line up. This process is subsequently repeated for all the spectra that are to be stitched together.

5.2.2 Uncertainty Estimation

An estimate in the uncertainty of a wavelength value for a peak coming from the measured spectral data is derived from the optical apparatus function. The optical apparatus function is the spectra that is recorded with the experimental setup for a narrow singular emission line. This was done for the x-axis calibration with the Hg(Ar)-lamp (see 4.3.2) and that same data can be used. The obtained curves for such an emission line are then fitted with a normalized Gaussian Profile:

$$G(\lambda) = \frac{2}{\Delta_{app}\sqrt{\pi}} e^{-\frac{(\lambda - \lambda_0)^2}{(\Delta/2)^2}}$$
(5.1)

where λ_0 is the wavelength location of the maximum. The apparatus function width Δ_{app} , which is the full width at 1/e (roughly 0.37) of the maximum of the resulting Gaussian Profile, is then the estimated uncertainty in wavelength. Figure 5.2 shows the performed fit and the resulting apparatus function width for the 600 GRT.



FIGURE 5.2: Measured peak response and performed Gauss fit

Three uncertainties for the three gratings are determined this way:

 $\Delta_{app150GRT} = 0.99 \text{ nm}$ $\Delta_{app600GRT} = 0.25 \text{ nm}$ $\Delta_{app1800GRT} = 0.08 \text{ nm}$

As expected, the uncertainty decreases for the finer gratings due to the higher linear dispersion.

5.3 High-speed Video Analysis

The videos recorded with the FASTCAM camera using the PFV software are saved as .AVI files. Since the videos are recorded at frame rates of up to 3600 fps, these files quickly reach large sizes. Before results can be presented, it is necessary to explain what type of information was extracted from the video data and how this was done.

5.3.1 Determining Delay Times

The main use of the recorded video footage is to determine the ignition delay time of the mixing and combustion process. To achieve that, the time stamps of the relevant frames are determined. This is done using the header in the video file that contains information on the current time and date, the frame rate and most importantly the elapsed time since the recording started (see fig. 5.3a).

Three time stamps are determined for every drop-test recorded:

1. t_0 (fig. 5.3c): This is the time at which the drop first touches the surface of the liquid at the bottom of the bowl. It is a clearly identifiable event and its uncertainty σ_{t_0} is estimated to be equal to the time difference Δt between two frames. That time difference is determined by the frame rate of the recording, as it is equal to the reciprocal value of it:

$$\sigma_{t_0} = \Delta t = \frac{1}{\text{fps}} \tag{5.2}$$

2. t_v (fig. 5.3d): This is the time at which pre-ignition vapors start to form and expand in an explosive manner. Its time stamp is less clearly defined and its uncertainty thus estimated to be equal to the duration of two frames.

$$\sigma_{t_v} = 2\Delta t = 2\sigma_{t_0} \tag{5.3}$$

FASTCAM SA-X2 type	480K	3600 fps
1/3613 sec	768 x 1016	Start
frame : 25839	+7177.500 ms	Date : 2019/10/15
Time : 11:09		

(a) Example of a header in the recorded .AVI file



(b) Drop approaching the liquid surface



(d) Explosive preignition vapor forming, defined as $t_{\boldsymbol{v}}$



(c) The point of contact, defined as t_0



(e) Ignition, defined as t_i

FIGURE 5.3: The typically acquired time stamps of a drop event (here of HTP and EMIM SCN).

3. t_i (fig. 5.3e): This is the time at which ignition occurs in the vapor. This event is clearly identifiable by a glowing spot or flame kernel and is thus estimated to have the same uncertainty as t_0 .

To obtain these time stamps, the video has to be watched frame for frame to determine the exact moments the described events occur. This process is quite time consuming and hard to automize, which is probably the biggest disadvantage of this method.

In accordance with the theoretical model and definitions discussed in chapter 2.1.2, the total ignition delay time IDT is then calculated with

$$IDT = t_i - t_0 \tag{5.4}$$

According to Gaussian error propagation, its uncertainty is

$$\sigma_{\rm IDT} = \sqrt{\sigma_{t_0}^2 + \sigma_{t_i}^2} = \sqrt{2\sigma_{t_0}^2} = \sqrt{2}\sigma_{t_0} = \frac{\sqrt{2}}{\rm fps}$$
(5.5)

Similarly, the chemical delay time τ_{chem} and the physical delay time τ_{phys} can be determined.

$$\tau_{phys} = t_v - t_0 \qquad \text{and} \qquad \tau_{chem} = t_i - t_v$$

$$(5.6)$$

Their uncertainties are

$$\sigma_{\tau_{phys}} = \sigma_{\tau_{chem}} = \sqrt{\sigma_{t_{0/i}}^2 + \sigma_{t_v}^2} = \sqrt{\sigma_{t_{0/i}}^2 + 2\sigma_{t_{0/i}}^2} = \sqrt{3\sigma_{t_{0/i}}^2} = \frac{\sqrt{3}}{\text{fps}}$$
(5.7)

These uncertainties only represent the systematic error σ_s of a single measurement. Typically, multiple tests are performed at theoretically identical test conditions and an average of the obtained delay times is calculated. To quantify the statistical uncertainty coming from the spread in results in a set of tests, the confidence interval \overline{s} is calculated with

$$\overline{s} = \frac{s}{\sqrt{n}} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{n \cdot (n-1)}}$$
(5.8)

where s is the standard deviation, x_i are the determined values (in this case IDT, τ_{chem} or τ_{phys}), \overline{x} is the average of said values and n the total number of values determined. The total uncertainty of the obtained average is the Pythagorean sum of the systematic and the statistical error:

$$\sigma_{\overline{\text{IDT}}/\bar{\tau}_{phys}/\bar{\tau}_{chem}} = \sqrt{\sigma_{\overline{\text{IDT}}/\tau_{phys}/\tau_{chem}}^2 + \bar{s}^2}$$
(5.9)

5.3.2 Determinining Drop Size and Speed

Apart from ignition delay time determination, the video footage is also used to determine the size and speed of the drop. This can be done by using the known size of the glas dish, that is captured as part of the recording, to determine a conversion factor CF in px/mm. An example is given in figure 5.4.



FIGURE 5.4: Data acquired from video screenshots for drop size and speed determination

For a diameter D_b of the bowl in pixels (px), the conversion factor is calculated with

$$CF = \frac{D_b}{50} \left[\frac{\mathrm{px}}{\mathrm{mm}}\right] \qquad \text{with} \qquad \sigma_{CF} = \frac{\sigma_{D_b}}{50}$$
(5.10)

The watch glass dish for all experiments has a diameter of 50 mm. An uncertainty of $\sigma_{D_b} = 3 \text{ px}$ when determining the diameter is assumed. A drop with diameter D_d in px can then be transferred to mm:

$$D_d \,[\mathrm{mm}] = \frac{D_d \,[\mathrm{px}]}{CF} \qquad \text{with} \qquad \sigma_{D_d} = \sqrt{\left(\frac{\sigma_{D_d [px]}}{CF}\right)^2 + \left(\frac{D_d}{CF^2}\sigma_{CF}\right)^2} \tag{5.11}$$

Its uncertainty is calculated according to Gaussian error propagation. $\sigma_{D_d}[px]$ is also assumed to be 3 px. Finally, assuming its shape to be spherical, the drop volume and its uncertainty can be calculated :

$$V_d = \frac{1}{6}\pi D_d^3 \qquad \text{with} \qquad \sigma_{V_d} = \frac{1}{2}\pi D_d^2 \sigma_{D_d} \tag{5.12}$$

This procedure is repeated for multiple images and an average is calculated. The systematic uncertainty for one measurement is then again added to the confidence interval in a Pythagorean sum to give the uncertainty of the average.

An estimate of the speed of the drop can be calculated by noting the pixel position and the time stamp of the drop at two different times before impact $(x_1,y_1,t_1 \text{ and } x_2,y_2,t_2 \text{ respectively})$. The distance s between the two points in pixel can then be calculated using

$$s[px] = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}$$
 (5.13)

That distance can be transferred to mm using the previously determined conversion factor. The speed of the drop is then calculated with

$$u_{dr} = \frac{s \,[\text{mm}]}{t_2 - t_1} \tag{5.14}$$

Of course, this only represents a rough estimate of the impact speed, as it assumes a constant speed between the two points. In reality, the drop is accelerated.

6 Test Results and Discussion

As part of this thesis, first drop tests are performed to ensure the correct functionality of the setup as well as analyze the impact of different physical and chemical factors on the combustion process in general and on the ignition delay time. Concurrently, various spectra with different settings are recorded to look for interesting spectral features that could be further analyzed in the future. In total, over 160 drop tests were conducted using the HYPED UP.

6.1 Preliminary Pressure Tests

During first drop tests with HTP under lower pressure at around 0.5 bar, drops would sporadically form at the canula tip without the actuator or syringe moving. The same, however, did not occur for the ionic liquids. This prevented any further testing under low-pressure conditions, as it could cause unwanted ignition. The reason for this behavior is believed to be the outgassing of oxygen in the HTP which leads to an expansion of the total volume in the syringe. Since the syringe is fixed in place and cannot move, this volume expansion leads to HTP getting pushed out of the canula. A possible solution is to introduce a valve in between the syringe and the canula that is only opened shortly before a test is run.

The chamber was also closed completely and drop-tests were performed to measure the resulting peaks in pressure and ensure that the chamber was able to withstand them. Pressure peaks at around 1.05 bar absolute were measured. These did not pose a problem for the chamber and no damage or leaks were detected.

6.2 Delay Time Determination and Combustion Analysis

The following matrix summarizes all the different test types that were performed with variations in oxidizer or fuel amount, drop height and the order in which is dropped. The oxidizer used for these tests was HTP (Propulse® by EVONIK) with a concentration of 96.1 %. The fuel used is the ionic liquid EMIM SCN provided by Iolitec with varying amounts of copper added as a catalyst. All tests are performed at ambient pressure and temperature.

Variation No.	No. of tests	Catalyst	Order	Average Fuel amount [µl]	Average Ox. amount [µl]	Drop height [mm]
1	24	none	O. on F.	115.3 ± 2.0	13.9 ± 2.3	61
2	10	none	F. on O.	14.4 ± 2.0	88.0 ± 1.9	61
3	33	none	O. on F.	115.3 ± 2.0	11.0 ± 1.9	61
4	8	none	O. on F.	57.7 ± 2.0	13.9 ± 2.3	61
5	25	$1~{\rm wt}\%$ Cu	O. on F.	115.3 ± 2.0	13.9 ± 2.3	61
6	20	$5~{\rm wt}\%$ Cu	O. on F.	115.3 ± 2.0	13.9 ± 2.3	61
7	20	none	O. on F.	115.3 ± 2.0	13.9 ± 2.3	141

TABLE 6.1: Test matrix showing the different variations that were tested

One test typically consisted of 3 to 8 ignitions, where only the first two are recorded with the camera and all others are used for spectroscopy. Variation number 1 was used as a baseline test

and all other variations differ in one factor compared to it. This allows to isolate the impact of that said factor on IDT and combustion.

The variation in propellant amount and drop height of the component that is dropped was achieved using one of three canulas: 1.1 mm x 40 mm, 1.1 mm x 120 mm and 0.8 x 120 mm (given as canula diameter x length). These result in the following drop sizes and uncertainties for HTP and EMIM (see ch. 5.3.2):

$\emptyset_{\text{canula}} \text{ [mm]}$	D_{EMIM} [mm]	$V_{\rm EMIM}$ [µl]	D_{HTP} [mm]	$V_{\rm HTP}$ [µl]
0.8	3.0 ± 0.2	14.4 ± 2.0	2.8 ± 0.2	11.0 ± 1.9
1.1			2.9 ± 0.4	13.9 ± 5.7

TABLE 6.2: The determined drop sizes

The same canula diameter results in slightly larger EMIM drops, which is due to its higher surface tension. Furthermore, the smaller canula produces a more reliable drop size overall. The variation in propellant amount of the component that is pre-dropped can be varied simply by changing the number of drops.

For all tests, the discussed time stamps were determined for the first two ignitions.

Establishing a Baseline (Var. 1)

For these baseline tests, 8 drops of EMIM SCN created with the 0.8 mm diameter canule were pre-dropped onto the dish for a total of 115 μ l. Using the 120 mm long canule with a diameter of 1.1 mm, a HTP drop was dropped onto it from a height of around 61 mm. A total of 24 of these tests were carried out. The image series in figure 6.1 shows what a typical ignition process looks like.

The time of impact is set to t = 0 ms for the image series (fig. 6.1b). After impact, a wavelike ripple structure is visible on the liquid surface and mixing occurs (fig. 6.1c). The increase in temperature caused by the exothermic chemical reaction eventually leads to an explosive vapor outburst. For this drop series, it was typical for the outburst to occur at two points at the same time both slightly off-center (fig. 6.1d). The vapor continues to spread out and heat up until ignition occurs at one point in the vapor (also referred to as a 'flame kernel', fig. 6.1e). The flame then rapidly propagates through the entire vapor cloud (fig. 6.1f) and continues spreading out until maximum flame development is reached (fig. 6.1g). Eventually, the flame dwindles down.

Variation No.	$IDT_1 [ms]$	$\tau_{chem_1} \; [ms]$	$IDT_2 [ms]$	$\tau_{chem_2} \; [\mathrm{ms}]$
1	31.3 ± 3.8	3.2 ± 1.1	14.1 ± 2.6	2.2 ± 0.7

TABLE 6.3: Results of the baseline test

Table 6.3 shows the obtained results that will act as a baseline to which all other variations are compared. The chemical delay time makes up roughly 10 % of the IDT_1 . The second measured ignition delay time is less than half of IDT_1 . This can most likely be attributed to the increased temperature and consequential increase in reactivity of the fuel. This pattern is seen throughout all test variations.



FIGURE 6.1: Image series capturing hypergolic ignition between HTP and EMIM SCN

Effect of Drop Order (Var. 2)

For test variation number 2, the drop order was changed and fuel is dropped onto the oxidizer. Eight drops of HTP were pre-dropped with the smaller canula resulting in a total oxidizer volume of around 88 µl.

Variation No.	Drop Order	$IDT_1 [ms]$	$\tau_{chem_1} \; [ms]$	$IDT_2 [ms]$	$\tau_{chem_2} \; [\mathrm{ms}]$
1	O. on F.	31.3 ± 3.8	3.2 ± 1.1	14.1 ± 2.6	2.2 ± 0.7
2	F. on O.	65.3 ± 7.0	3.5 ± 1.3	32.9 ± 4.4	4.8 ± 2.0

TABLE 6.4: Results for variation of the drop order

The impact on both the ignition delay time as well as its uncertainty are significant, with an increase of more than 100% in the former. The same holds true for the second delay time. Interestingly enough, however, the chemical delay time τ_{chem} remains almost the same. This indicates that it takes longer for the required heat to build up, yet once vaporization is reached ignition follows equally as fast.

Effect of Oxidizer and Fuel Amount (Var. 3 & 4)

In order to analyze the effect of the amount of oxidizer and fuel, two test variations were performed. In one, the HTP is dropped using the long canula with a diameter of 0.8 mm instead of 1.1 mm. This lowers the oxidizer drop volume by around 20% (Var. 3). In variation four, 4

Variation No.	O/F	$IDT_1 [ms]$	$\tau_{chem_1} \; [ms]$	$IDT_2 [ms]$	$\tau_{chem_2} \; [\mathrm{ms}]$
1	0.12	31.3 ± 3.8	3.2 ± 1.1	14.1 ± 2.6	2.2 ± 0.7
3 4	0.09 0.24	29.8 ± 2.9 30.4 ± 2.5	3.2 ± 0.8 3 4 ± 0.8	15.8 ± 2.8 14.3 ± 2.3	2.2 ± 0.7 2.3 ± 0.7
$\frac{3}{4}$	$\begin{array}{c} 0.09 \\ 0.24 \end{array}$	$\begin{array}{c} 29.8 \pm 2.9 \\ 30.4 \pm 2.5 \end{array}$	$3.2 \pm 0.8 \\ 3.4 \pm 0.8$	15.8 ± 2.8 14.3 ± 2.3	$2.2 \pm 0.$ $2.3 \pm 0.$

instead of 8 drops of fuel are pre-dropped, lowering the fuel amount by 50% down to 58μ l.

TABLE 6.5: Results for variation of the oxidizer to fuel ratio

Both changes only have a small impact on the IDT or the chemical delay time. All lie within the area of uncertainty of the others. The same goes for IDT₂ and τ_{chem_2} . However, a decrease in uncertainty is visible, most significantly in variation 4. In this variation, the fuel pool amount was reduced by 50%. It seems, this lowers the impact of kinematic effects during mixing and thus the spread in IDT values.

Effect of Copper Catalyst (Var. 5 & 6)

In these test runs, CuSCN copper(I)-thiocyanate was added to the EMIM fuel as a catalyst. As discussed in 2.1.3, this is expected to enhance the chemical reaction. Figure 6.2 shows a typical ignition process of 1 wt% CuSCN dissolved in the fuel.



FIGURE 6.2: Image series capturing hypergolic ignition between HTP and EMIM SCN + 1 wt% CuSCN

The most visible and obvious difference at first glance is the change in flame color, which now has a green hue to it. The point of ignition is much less localized and more spread out than in the baseline measurement and occurs much faster (Fig. 6.2e). It follows faster after the the onset of vaporization (Fig. 6.2d) and is thus typically closer to the surface of the fuel. Figure 6.2f shows a brighter more intense area at the core of the flame that violently burns outwards and eventually detaches. This phenomenon was common for this test variation.



FIGURE 6.3: Image series capturing hypergolic ignition between HTP and EMIM SCN + 5 wt% CuSCN

When adding more catalyst, the green color of the flame gets even more intense (fig. 6.3). Ignition occurs even faster and more violently and the flame gets much brighter, resulting in overexposure of the camera (Fig. 6.3d). Unfortunately, even if the aperture was closed completely, the image still overexposed. The increase in brightness and intensity of the combustion hints towards an increase in flame temperature.

Figure 6.4 shows all the determined IDT data points for the baseline measurement (red), with 1 vol% Cu (blue) and with 5 vol% Cu (green) as well as the resulting average and uncertainty. Plotting the data-points this way visualizes how, with an increase in Cu catalyst, not only the average IDT sinks but also the spread in points and therefore the resulting uncertainty decreases.



FIGURE 6.4: All acquired IDT data points for test variations 1,5 and 6

Table 6.6 shows an IDT decrease of around 50% for an added 1 wt% Cu catalyst, however only a decrease of around 18% for another 4 wt% more catalyst. This trend hints towards a maximum

Variation No.	Catalyst	$IDT_1 [ms]$	$\tau_{chem_1} \; [ms]$	$IDT_2 [ms]$	$\tau_{chem_2} \; [\mathrm{ms}]$
1	none	31.3 ± 3.8	3.2 ± 1.1	14.1 ± 2.6	2.2 ± 0.7
5 6	1 vol% Cu 5 vol% Cu	$\begin{array}{c} 16.2 \pm 2.0 \\ 13.3 \pm 1.1 \end{array}$	$1.4 \pm 0.7 \\ 0.6 \pm 0.6$	$12.6 \pm 2.6 \\ 9.8 \pm 1.5$	$\begin{array}{c} 0.9 \pm 0.6 \\ 0.5 \pm 0.6 \end{array}$

of achievable decrease in IDT through catalyst additives. The chemical delay time follows the same trend, going as low as 0.6 ms for the test with an added 5 wt% in Cu. The same goes for both IDT₂ and τ_{chem_2} .

TABLE 6.6: Results for varying Cu catalyst proportions

Effect of Drop Height/Impact Speed (Var. 7)

The last effect that was analyzed was the drop height, which of course effects the speed at drop impact. To achieve this, a shorter canula with the same diameter of 1.1 mm is used. This doubled the impact speed from $\sim 0.8 \ m/s$ to $\sim 1.6 \ m/s$. Table 6.7 shows the results.

The average IDT remains almost the same, however the uncertainty increases substantially by about 70 %. Figure 6.5 shows how a much wider spread in measured IDTs causes this increase. A possible explanation is that the higher impact speed causes more extreme fluid dynamical movement upon impact. This can either benefit or hinder mixing depending on the exact impact location.

Variation No.	$u_{dr} \mathrm{[m/s]}$	$IDT_1 [ms]$	$\tau_{chem_1} \; [ms]$	$IDT_2 [ms]$	$\tau_{chem_2} \; [\mathrm{ms}]$
1	0.8	31.3 ± 3.8	3.2 ± 1.1	14.1 ± 2.6	2.2 ± 0.7
7	1.6	31.0 ± 6.5	4.2 ± 1.5	11.0 ± 4.9	2.3 ± 0.9

TABLE 6.7: Results for variation of drop height



FIGURE 6.5: All acquired IDT data points for variation 1 (red) and 7 (blue)

Summary

Figure 6.6 gives an overview of all measured average ignition delay times of the different test variations including its uncertainty. Each IDT is further divided into physical and chemical delay time (as defined in 2.1.2).



FIGURE 6.6: The resulting IDT averages for the different test variations

Based on these results, it is recommended to perform drop tests with smaller oxidizer drops onto a smaller amount of fuel at lower impact speeds to get the most accurate results. This reduces the effect of mixing that seems to have the largest impact on the uncertainty, as seen in test variations 3,4 and 7.

6.3 Spectroscopy

Measuring the spectra was not a trivial task, as data collection can be quite complicated with various settings that impact the obtained results. For every spectra measured, it is desireable to make use of the entire intensity range. This means that a number of measurements must be made for every spectra to determine the correct gain and exposure settings for that specific spectra. With a constant light source, this does not pose a problem. In this case, however, light emitted in a time period < 100 ms is to be analyzed. For this reason, typically multiple ignitions events were recorded in a row.

6.3.1 Spectra Slit Width Influence

In a series of tests with a variation in the slit width of the spectroscope, the impact on resulting spectra was analyzed. The three spectra depicted in figure 6.7 were all taken with the same settings and grating at the same central wavelength (in this case CW = 310 nm and GRT = 600 g/mm). All necessary correction steps (5.2) were already performed, except for baseline correction.



FIGURE 6.7: The same spectra recorded with three different slit widths

The increase in spectral resolution for a smaller slit width is clearly visible. What looks to be an underlying continuous spectrum at 310 nm actually turns out to be a group of many peaks (in this case the OH band, more on that in the next section). The smaller the slit width is, the more of these become visible. However, a smaller slit width also means a loss in signal intensity. This can be seen by the increase in noise of the spectra, as its relative intensity compared to the signal increases.

6.3.2 Comparing Flame Emission Spectra

By stitching together and summing up multiple spectral measurements, three spectra for the hypergolic flame emission of HTP and EMIM SCN with varying degrees of Cu SCN added were obtained. The 600 g/mm grating was used as it is a good middle ground between the other two gratings, providing sufficient linear dispersion without too large of a signal loss. Each of these spectra consists of data from at least 50 ignition events. Figure 6.8 shows the entire spectra for the hypergolic reaction between HTP and EMIM SCN and between HTP and EMIM SCN + 5 wt% CuSCN. The second spectra is then shown again with a smaller y-axis section in order to enhance the visibility of smaller peaks and features.

Both spectra show an intense peak at around 589 nm and a pair of peaks at around 765 nm. These are the emissions lines of sodium (Na) and potassium (K). The sodium line is what gives the flame its typical orange-yellowish color. The potassium lines are outside of the visible



(c) HP and EMIM SCN + 5% Cu flame emission close-up

FIGURE 6.8: Stitched spectra recorded with the 600 g/mm grating

wavelength range. Both of these lines hint towards traces of sodium and potassium in the pure EMIM SCN fuel. These are most likely residues from the IL synthesis. Clearly visible in the spectrum of the ignition with added copper (fig. 6.8b/ 6.8c) is the increase in intensity in the green wavelength region (500 - 565 nm), although its maximum value is only around 10 % of the Sodium peak. For an added Cu-catalyst of just 1%, the green intensity is only around 5% of the sodium peak. That difference in intensity of the green light for the different fuel versions is also visible in the image series (fig. 6.1 - 6.3).

Alkali Metals

A closer look is taken at the sodium and potassium lines. Both of these are the fluorescent emission lines of alkali metals. The sodium line is actually a double line, also know as the D_1 and D_2 lines of the sodium doublet. Figure 6.9 shows the recorded peaks with the three available gratings as well as the peak locations.



FIGURE 6.9: The Na-doublet recorded with the three gratings

The potassium emission lines were also recorded with a finer grating. A third alkali line, that of lithium, was also discovered. Its intensity is only a fraction of the Na-doublet, which is why it does not stand out when viewing the entire spectrum. This line is also a doublet in reality, however even the finest grating does not have a high enough linear dispersion to resolve it.



FIGURE 6.10: K-doublet



Table 6.8 lists the literature values of all three Alkali emission doublets and the values measured in the flame emission. Research has been conducted that demonstrated the temperature, pressure and equivalency ratio dependency of fluorescence alkali spectral signals [24, 32]. The appearance of these lines in the measured hypergolic combustion spectra could potentially be made use of in a similar way to determine certain flame characteristics.

	literature value [nm]	measured value [nm]			literature	measured
Na [57]	589.00	588.92 ± 0.08			value [nm]	value [nm]
	589.59	589.52			324.76	324.81 ± 0.08
Li [58]	670.78	670.75 ± 0.08		Cu [60]	327.40	327.47 ± 0.08
	670.79		-		510.56	510.62 ± 0.08
K [59]	766.49	766.42 ± 0.08		CuO [60]	604 - 616	604 - 616
	769.90	769.81 ± 0.08	_			

 TABLE 6.8: Literature and measured spectroscopic

 data of alkali fluorescence lines

Copper Occurrences

As expected, the spectra recorded of the ignition event with added Cu-catalyst contains various peaks related to copper or other molecules that contain it. Table 6.9 lists those lines that were identified. Figure 6.12a and 6.12b show the three measured copper emission lines. Figure 6.12c shows the widely spaced double headed copper(II) oxide band observed at around 610 nm.

6.3.3 OH Band

A large part of the spectral measurements were focused on the OH band at around 306 nm in the UV region of the flame emission, as a temperature dependence of the intensity ratio off the emission lines within this band has been repeatedly investigated [29, 30].

Figure 6.13 shows a side by side comparism of an obtained spectrum with the 1800 g/mm grating of the OH band (that again consists of multiple measurements added up) and the theoretically

TABLE 6.9: Literature and measured spectroscopic

 data of copper lines



FIGURE 6.12: Recorded spectral traces of copper

predicted OH band spectrum for various gas temperatures (taken from [29]). The peaks typically used for temperature determination in the OH band due to their greater intensity are labeled G_0 , G_1 and G_{ref} . They are clearly visible in the measured data.



FIGURE 6.13: Comparism of recorded and simulated highly-resolved OH band

The same goes for a recorded spectrum with the 600 g/mm grating when compared with actually recorded OH band spectral data of an argon plasma jet (fig. 6.14) [29].

The flame temperature is dependent on the ratio of G_0/G_{ref} or G_1/G_{ref} and the apparatus function width Δ_{app} . Generally speaking, a higher value of either ratio indicates a higher flame temperature. Figure 6.15 shows three recorded OH bands for ignition between HTP and EMIM SCN with an increase in Cu-catalyst from left to right. The intensity is normed to G_{ref} . A clear increase in intensity of peak G_1 with respect to G_{ref} is observed.

	$0~{\rm wt}\%$ CuSCN	$1~{\rm wt}\%$ CuSCN	$5~{\rm wt}\%$ CuSCN
I _{G1} [a.u.] T [K]	$\begin{array}{c} 0.77 \\ 2800 \end{array}$	0.79 2900	$0.86 \\ 3300$
- []	2000	2000	0000

TABLE 6.10: The relative intensity of peak G_1 in the OH bands

This indicates an increase in flame temperature, which coincides with the observed increase in brightness and intensity of the combustion in the high speed recordings. Using the tables provided in [29], the temperatures can be determined. These values are to be understood as a







FIGURE 6.15: OH Band of ignition between HTP and EMIM SCN with varying wt% of Cu catalyst

qualitative statement rather than accurate temperature measurements, since it is not clear if the measurements made in the source on laminar plamsa flames are directly applicable to this case.

7 Summary and Outlook

Hypergolic fuels have been used in space-flight since the 1960s. Their characteristic of selfigniting upon contact between oxidizer and fuel eliminates the need for an ignition system. This simplifies the engine design. Furthermore, they have good storage properties. However, conventional hypergolic fuels such as monomethylhydrazine (MMH) and nitrogen tetroxide (NTO) are notoriously toxic and therefore expensive in handling. At the Insitute of Space Propulsion of the German Aerospace Center (DLR), research is being conducted on novel green fuels that could replace hydrazine in the long term. A possible promising combination is highly concentrated hydrogen peroxide (HTP) as an oxidizer with ionic liquids (IL) as a fuel.

An important property of hypergolic propellants is their ignition delay time (IDT). This is defined as the time between initial contact between the two components and first appearance of a flame. An IDT that is too long can lead to a hard start or even destruction of the engine. A simple method to determine the IDT is the so called drop-test. In addition, an investigation of the general ignition sequence and combustion regime is of interest, as these are still largely unexplored, especially for green hypergolic fuels.

Within the scope of this thesis, a test bench including a reaction chamber was developed, constructed, assembled and put into operation that allows for the simple and reliable performance of drop-tests on conventional and novel green propellants. The determination of the ignition delay time and general combustion analysis are carried out with a high speed video camera. In addition, the emitted light of the flame is spectroscopically examined in order to draw conclusions on reaction partners, intermediate products and flame temperature.

The first task was to determine the exact boundary conditions and requirements and their influence on the chamber design. For this purpose, an extensive literature study on the subject of hypergolicy, drop-tests and spectroscopy was carried out and various possible chamber designs were identified. The final design consists of a 15 x 15 cm square tube with a wall thickness of 5 mm whose ends are sealed with 10 mm thick plates. On three sides, openings are milled into the tube, onto which UV-transparent quartz glass panes are clamped down on with a frame. One of the sides can be removed for easy access to the inside of the chamber. The fuel is introduced via cannulas in combination with syringes, which can be moved by two linear motors. The chamber has been designed to withstand vacuum down to 0.3 bar, which is generated by a vacuum pump. Dropping and ignition is carried out on a watch glass bowl. The bowl can be rotated and rinsed with water using a solenoid valve in combination with a nozzle if required.

In the next step, the necessary measuring and control technology of the test bench was set up and calibrated. The control of the motors and the valve as well as the temperature and pressure recording of the chamber interior is carried out using the NI-cDAQ system via LabVIEW. The SP2750 Czerny-Turner spectrometer was calibrated using a Hg(Ar) lamp and device curves were determined for the setup with a tungsten halogen lamp. The triggering of the spectroscope at the onset of ignition is done by the camera. The necessary corrections and the evaluation of the spectral data were implemented and automated in Matlab routines.

The test bench was successfully put into operation with more than 150 drop tests of hydrogen peroxide and the ionic liquid 1-ethyl-3-methylimidazolium-thiocyanate (EMIM SCN). The impact of different parameters on the ignition delay was investigated. The results are summarized in table 7.1

In addition, different amounts of copper(I)-thiocyanate (CuSCN) were added to the IL as a catalyst and the influence on the ignition process and the IDT were investigated. An addition

Parameter	Outcome
Drop order	Ox. on Fu.: IDT and uncertainty more than twice as high. Little impact on chemical delay time.
Ox./Fu. amount	Little impact on IDT. Smaller fuel quantities in the bowl reduce uncertainty.
Drop height	Little impact on IDT. Increase in uncertainty by ~ 70 %.
1. vs 2. IDT	Second IDT on average less than 50 $\%$ of the first.

TABLE 7.1: Influence of test parameters on IDT

of 5 wt% CuSCN reduced the mean ignition delay time from 31.3 ± 3.8 ms to 13.3 ± 1.1 ms. The spectra were used to identify traces of sodium and potassium in the flame emission, which produced strong emission peaks. A closer examination of the OH band at about 306 nm showed a correlation between flame temperature and the ratio of intensity of certain spectral lines. Further experiments should be performed under vacuum and with conventional fuels. In addition, it would be interesting to investigate the flame emission spectrally resolved over time. Using a high speed camera in combination with a band-pass filter, certain spectral ranges such as the OH range including the OH* radical could be visualized. The recording of streaks and absorption spectra would also be of interest and could further contribute to the understanding of hypergolic ignition processes.
Bibliography

- Yanqiang Zhang et al. "Ionic liquids as hypergolic fuels". In: Angewandte Chemie International Edition 50.41 (2011), pp. 9554–9562.
- [2] Wojciech Florczuk and Grzegorz Rarata. "Assessment of various fuel additives for reliable hypergolic ignition with 98%+ HTP". In: 66th International Astronautical Congress. International Astronautical Federation Jerusalem. 2015.
- [3] ECHA updates the REACH Candidate List. June 2011. URL: https://echa.europa.eu/ de/-/echa-updates-the-reach-candidate-list.
- [4] K Kishore and MR Sunitha. "Correlation of Specific Impulse and Ignition Delay in Liquid Rocket Propellants". In: *Propellants, Explosives, Pyrotechnics* 2.5 (1977), pp. 98–99.
- [5] Armin Dadieu, Ralf Damm, and Eckart W Schmidt. Raketentreibstoffe. Springer-Verlag, 2013.
- [6] Irvin Glassman, Richard A Yetter, and Nick G Glumac. *Combustion*. Academic press, 2014.
- [7] Guenter Spengler and Albert Lepie. Rocket Propellants with Hypergolic Properties. I. Method of Measuring Ignition Delay. II. Ignition Delay of Fluid Propellant Combinations with Nitric Acid as Oxidizer. Tech. rep. Deutsche Versuchsanstalt fuer Luft- und Raumfahrt Ev Munich, 1962.
- [8] MA Pino. "A versatile ignition delay tester for self-igniting rocket propellants". In: Journal of Jet Propulsion 25.9 (1955), pp. 463–467.
- [9] Jan Witte. "Design and experimental investigation of injectors for green hypergolic propellants". MA thesis. University of Stuttgart, 2019.
- [10] Angelo J Alfano, Jeffrey D Mills, and Ghanshyam L Vaghjiani. "Highly accurate ignition delay apparatus for hypergolic fuel research". In: *Review of scientific instruments* 77.4 (2006), p. 045109.
- [11] John Blevins, Rudy Gostowski, and Silvio Chianese. "An experimental investigation of hypergolic ignition delay of hydrogen peroxide with fuel mixtures". In: 42nd AIAA Aerospace Sciences Meeting and Exhibit. 2004, p. 1335.
- [12] Sh L Guseinov et al. "Hypergolic propellants based on hydrogen peroxide and organic compounds: historical aspect and current state". In: *Russian Chemical Bulletin* 67.11 (2018), pp. 1943–1954.
- [13] Stephen M Davis and Nadir Yilmaz. "Advances in hypergolic propellants: Ignition, hydrazine, and hydrogen peroxide research". In: Advances in Aerospace Engineering 2014 (2014).
- [14] Robert K Palmer and John J Rusek. "Low-Toxicity Reactive Hypergolic Fuels for Use with Hydrogen Peroxide". In: *ESA Special Publication*. Vol. 557. 2004.
- [15] Brian Melof and Mark Grubelich. "Investigation of hypergolic fuels with hydrogen peroxide". In: 37th Joint Propulsion Conference and Exhibit. 2001, p. 3837.
- [16] Elena Sebastiao et al. "Recent developments in the field of energetic ionic liquids". In: Journal of Materials Chemistry A 2.22 (2014), pp. 8153–8173.

- [17] Jairton Dupont and László Kollár. Ionic Liquids (ILs) in Organometallic Catalysis. Vol. 51. Springer, 2015.
- [18] Nick Zarbo, Hatem Belal, and Timothee L Pourpoint. "Effect of Water and Humidity on Hypergolic Propellant Ignition Delay". In: 51st AIAA/SAE/ASEE Joint Propulsion Conference. 2015, p. 3867.
- [19] Wojciech Florczuk and Grzegorz P Rarata. "Performance evaluation of the hypergolic green propellants based on the HTP for a future next generation spacecrafts". In: 53rd AIAA/SAE/ASEE Joint Propulsion Conference. 2017, p. 4849.
- [20] Jianling Li et al. "Experimental observation of hypergolic ignition of superbase-derived ionic liquids". In: Journal of Propulsion and Power 34.1 (2017), pp. 125–132.
- [21] Xinyan Weng et al. "Coulomb explosion and ultra-fast hypergolic ignition of borohydriderich ionic liquids with WFNA". In: *Combustion and Flame* 194 (2018), pp. 464–471.
- [22] Thomas G Phillips and Jocelyn Keene. "Submillimeter astronomy (heterodyne spectroscopy)". In: Proceedings of the IEEE 80.11 (1992), pp. 1662–1678.
- [23] Sune Svanberg. Atomic and molecular spectroscopy: basic aspects and practical applications. Vol. 6. Springer Science & Business Media, 2012.
- [24] Michael J Mosburger. "Alkali Metal Spectroscopy for High-speed Imaging of Burned Gas Temperature, Equivalence Ratio and Mass Fraction Burned in Internal Combustion Engines." In: (2013).
- [25] Bohr's model of hydrogen. URL: https://www.khanacademy.org/science/physics/ quantum-physics/atoms-and-electrons/a/bohrs-model-of-hydrogen.
- [26] Martin Lauer and Thomas Sattelmayer. "On the adequacy of chemiluminescence as a measure for heat release in turbulent flames with mixture gradients". In: *Journal of Engineering* for Gas Turbines and Power 132.6 (2010), p. 061502.
- [27] Robert Klein, Steve Bublies, and Michael Oschwald. "Flame Emission Spectroscopy on a hypergolic NTO/MMH combustion". In: *MOTAR workshop, Toulouse*. 2012.
- [28] M Oschwald et al. "UNTERSUCHUNGEN ZUR ZERSTÄUBUNG UND VERBREN-NUNG IN KRYOGENEN LOX/H2-UND LOX/CH4-SPRAYFLAMMEN". In: ().
- [29] Charles De Izarra. "UV OH spectrum used as a molecular pyrometer". In: Journal of Physics D: Applied Physics 33.14 (2000), p. 1697.
- [30] S Pellerin et al. "A spectroscopic diagnostic method using UV OH band spectrum". In: Journal of Physics D: Applied Physics 29.3 (1996), p. 726.
- [31] Robert Stützer and Michael Oschwald. "The Hyperfine Structure of the OH* Emission Spectrum and its Benefits for Combustion Analysis". In: (2019).
- [32] Yuhe Zhang. "Temperature measurement in flames using TLAF, alkali emission and OH UV absorption". In: (2018).
- [33] Sebastian Knapp et al. "Emission Spectroscopy of the Combustion Flame of Aluminium/Copper Oxide Thermite". In: Propellants, Explosives, Pyrotechnics 44.1 (2019), pp. 9–17.
- [34] Wilfried Neumann. Fundamentals of dispersive optical spectroscopy systems. SPIE Press, 2014.
- [35] David Harvey DePauw University. 10.1: Overview of Spectroscopy. 2019. URL: https: //chem.libretexts.org/Courses/Northeastern_University/10:_Spectroscopic_ Methods/10.1:_Overview_of_Spectroscopy.

- [36] Newport Corporation. *Tutorial: Diffraction Grating Physics*. 2019. URL: https://www.newport.com/t/grating-physics.
- [37] Acton Series Monochromators and Spectrographs. Rev. N3.1. Princeton Instruments Spectroscopy group.
- [38] Dennis D Davis et al. "Fire, explosion, compatibility and safety hazards of hydrogen peroxide". In: (2005).
- [39] Reichelt Chemietechnik. Beständigkeitsliste. URL: https://www.rct-online.de/de/ RctBestaendigkeitsliste.
- [40] Canoga Park Rocketdyne. Hydrazine handling manual. Rocketdyne, 1961.
- [41] International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys. 1525 Wilson Boulevard, Arlington, VA 22209: The aluminum association, Feb. 2009.
- [42] Heinrich Dubbel and BJ Davies. Dubbel-Handbook of mechanical engineering. Springer Science & Business Media, 2013.
- [43] Alumero Group. EN AW-6060 Datasheet. July 2018.
- [44] Edmund Optics. The Correct Material for Infrared (IR) Applications. URL: https://www. edmundoptics.com/resources/application-notes/optics/the-correct-materialfor-infrared-applications/.
- [45] The Design of Pressure Windows. Crystan Ltd. https://www.crystran.co.uk/userfiles/files/design-of-pressure-windows.pdf, 2014.
- [46] Paul R Yoder Jr. Opto-mechanical systems design. CRC press, 2005.
- [47] Technical manual 2007: O-rings and static seals. Freudenberg Simrit GmbH. 2007.
- [48] NI cDAQ-9171/9174/9178 User Manual NI CompactDAQ USB 2.0 Chassis. National Instruments. July 2016.
- [49] ASTM Committee E-20 on Temperature Measurement and ASTM Committee E-20 on Temperature Measurement. Subcommittee E20. 04 on Thermocouples. *Manual on the use* of thermocouples in temperature measurement. Vol. 470. ASTM International, 1974.
- [50] FASTCAM SA-X2 High performance high-speed camera system Datasheet. Photron Europe Ltd. Feb. 2018.
- [51] CCD30-11 Front Illuminated Open Electrode High Performance CCD Sensor Datasheet. A1A-100008 Version 10. e2v Technologies Ltd. Sept. 2013.
- [52] Princeton Instruments/Acton. PI-MAX2: 1003 Datasheet Rev B5.
- [53] PIMAX Princeton Instruments. PI-MAX2 System Manual, Version 12. 2011.
- [54] Princeton Instruments. WinSpec Spectroscopy Software User's Manual Version 2.6A. Jan. 2012.
- [55] LOT-QuantumDesign. Pen-Ray light sources for wavelength calibration.
- [56] Vincent Mazet et al. "Background removal from spectra by designing and minimising a non-quadratic cost function". In: *Chemometrics and intelligent laboratory systems* 76.2 (2005), pp. 121–133.
- [57] JF Baugh et al. "Precision Stark spectroscopy of sodium 2 P and 2 D states". In: *Physical Review A* 58.2 (1998), p. 1585.
- [58] Leon J Radziemski, Rolf Engleman Jr, and James W Brault. "Fourier-transformspectroscopy measurements in the spectra of neutral lithium, I 6 and I 7 (Li I)". In: *Physical Review A* 52.6 (1995), p. 4462.

- [59] R Engleman. "unpublished wave number measurements 1999 quoted in M03". In: K: The uncertainty of the Ki 4p 2Po levels is probably less than 0.001 cm 1 (1999).
- [60] Reginald William Blake Pearse and Alfred Gordon Gaydon. *Identification of molecular spectra*. Chapman and Hall, 1976.

8 Deutsche Zusammenfassung

Hypergole Treibstoffe werden seit den 1960er Jahren in der Raumfahrt eingesetzt. Ihre Eigenschaft bei Kontakt zwischen Oxidator und Brennstoff spontan zu zünden, macht ein Zündsystem im Triebwerk überflüssig und vereinfacht dieses. Zudem zeichnen sie sich durch eine gute Lagerfähigkeit aus. Konventiolle hypergole Treibstoffe wie z.B. Monomethylhydrazin (MMH) und Stickstofftetroxid (NTO) sind jedoch sehr giftig und entsprechend aufwändig und teuer im Umgang. Am Institut für Raumfahrtantriebe des DLR wird deswegen an neuen sogennanten grünen Treibstoffen geforscht, die Hydrazin und seine Derivate langfristig ersetzen sollen. Eine mögliche vielversprechende Kombination ist hochkonzentrierter Wasserstoffperoxid als Oxidator in Kombination mit Ionischen Liquiden (IL) als Brennstoff.

Eine wichtige Eigenschaft hypergoler Treibstoffe ist ihr Zündverzug (ZV). Dieser ist definiert als die zeitliche Dauer zwischen Zusammentreffen der beiden Komponenten und erstem auftreten einer Flamme. Ein zu großer ZV kann zu einem sogenannten harten Start bis hin zur Zerstörung des Triebwerks führen. Eine einfache Methode, den ZV zu bestimmen ist der Tropftest. Darüber hinaus ist eine Untersuchung des allgemeinen Zündablaufs und der Verbrennung von Interesse, da diese vor allem für grüne hypergole Treibstoffe noch zu großen Teilen unerforscht sind.

Im Rahmen dieser Arbeit wurde ein Prüfstand mit einer Reaktionskammer entwickelt, konstruiert, aufgebaut und in Betrieb genommen. Der Aufbau ermöglicht eine einfache und zuverlässige Durchführung von Tropftest Versuchen an konventionellen und neuartigen grünen Treibstoffen. Die Zündverzugbestimmung und Verbrennungsuntersuchung erfolgt dabei mit Hochgeschwindigkeitaufnahmen. Zudem wird das emittierte Licht der Flamme spektroskopisch untersucht, um auf Reaktionspartner, Zwischenprodukte und Flammentemperatur Rückschlüssse ziehen zu können.

Zunächst galt es, die genauen Rahmenbedingungen und ihren Einfluss auf das Kammerdesign zu bestimmen. Dazu wurde eine ausgiebiege Literaturrecherche zu den Themen Hypergolität, Tropftests und Spektroskopie durchgeführt und es wurden verschiedene mögliche Kammerdesigns ermittelt. Das finale Design besteht aus einem 15 mal 15 cm großem Vierkantrohr mit einer Wanddicke von 5 mm dessen Enden mit 10 mm dicken Platten abgedichtet sind. In drei Seiten sind Öffnungen gefräst, über die UV durchlässige Quarzglasscheiben mit einem Rahmen angbracht sind. Eine der Seiten kann entfernt werden, um einen leichten Zugriff ins Innere der Kammer zu ermöglichen. Das Einbringen der Treibstoffe erfolgt über Kanülen in Kombination mit Spritzen, welche von zwei Linearmotoren verfahren werden können. Die Kammer wurde ausgelegt um einen Absolutdruck bis 0.3 bar standhalten zu können, welcher über eine Vakuumpumpe erzeugt wird. Die Zündung geschieht in einer Uhrglasschale. Diese kann rotiert und mit einem elektrisch schaltbaren Ventil in Kombination mit einer Düse bei Bedarf mit Wasser gespült werden.

Im nächsten Schritt wurde die nötige Mess- und Steuertechnik des Prüfstands aufgebaut und kalibriert. Die Ansteuerung der Motoren und des Ventils sowie Temperatur- und Druckaufzeichnung des Kammerinneren erfolgt über das NI-cDAQ System via LabVIEW. Das SP2750 Spektrometer vom Typ Czerny-Turner wurde mittels einer Hg(Ar) Lampe kalibriert und es wurden Gerätekurven für den Aufbau bestimmt. Das Triggern des Spektroskops bei Einsatz der Zündung erfolgt über die Kamera. Die nötigen Korrekturen und die Auswertung der Spektraldaten wurden in Matlab Routinen implementiert und automatisiert.

Der Prüfstand wurde mit insgesamt mehr als 150 Tropfversuchen von Wasserstoffperoxid und dem ionischen Liquid 1-Ethyl-3-methylimidazolium-thiocyanat (EMIM SCN) erfolgreich in Be-

Parameter	Einfluss
Tropfreihenfolge	Bei Oxidator auf Treibstoff: ZV und Unsicherheit mehr als doppelt so groß. Geringer Einfluss auf chemischen Zündver- zug.
Oxidator/Treib- stoffmenge	Kaum Einfluss auf ZV. Geringere Treibstoffmengen in der Schale reduzieren Unsicherheit.
Tropfhöhe	Geringer Einfluss auf Zündverzug. Zunahme der Unsicherheit um ${\sim}70$ %.
1. vs 2. ZV	Zweiter Zündverzug in der Regel weniger als 50 $\%$ des Ersten.

trieb genommen. Dabei wurde der Einfluss verschiedener Parameter auf den Zündverzug untersucht (siehe Tabelle 8.1).

TABELLE 8.1: Einfluss der getesteten Parameter auf den Zündverzug

Zudem wurden dem IL verschiedenen Mengen an Kupfer(I)-thiocyanat (CuSCN) als Katalysator beigemischt und der Einfluss auf den Zündvorgang und den ZV untersucht. Eine Zugabe von 5 Gew.-% CuSCN reduzierte den mittleren Zündverzug von 31.3 ± 3.8 ms auf 13.3 ± 1.1 ms. Anhand der Spektren konnten Spuren von Natrium und Kalium identifiziert werden, welche starke Emissionspeaks erzeugten. Eine nähere Untersuchung des OH-Bands bei ca. 306 nm zeigte ein Zusammenhang zwischen der Flammentemperatur und dem Verhältnis der Intensität gewisser Spektrallinien.

Weiterführend sollten Versuche unter Vakuum und mit konventiollen Treibstoffen durchgeführt werden. Zudem wäre es aussagekräftig, die Flammenemission zeitlich aufgelöst spektral zu untersuchen. Unter Verwendung einer Hochgeschwindikeitskamera in Kombination mit einem Bandpass-Filter könnten bestimmte Spektralbereiche wie z.B. der OH-Bereich inklusive des OH*-Radikals visualisiert werden. Auch die Aufnahme von Schlieren und Absorptionsspektren könnte weiter zum Verständnis hypergoler Zündprozesse beitragen.

9 Appendix



FIGURE 9.1: Acquired spectra of Hg(Ar) lamp with 600 g/mm grating



















