



**AP/KMnO₄ DUAL OXIDISER ON REDUCTION OF HCl GAS AND
COMBUSTION PROPERTIES FOR COMPOSITE SOLID ROCKET
PROPELLANT**

By

IZZAT NAJMI BIN MOHD YAACOB

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of
Philosophy**

January 2025

FK 2025 5

All material contained within the thesis, including without limitation text, logos, icons, photographs and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, written permission of Universiti Putra Malaysia.

Copyright © Universiti Putra Malaysia



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

**AP/KMnO₄ DUAL OXIDISER ON REDUCTION OF HCl GAS AND
COMBUSTION PROPERTIES FOR COMPOSITE SOLID ROCKET
PROPELLANT**

By

IZZAT NAJMI BIN MOHD YAACOB

January 2025

Chairman : Norkhairunnisa binti Mazlan, PhD

Faculty : Engineering

Composite solid propellant (CSP) is integral to modern rocketry and missile technology due to its high performance, reliability, and ease of use. Their applications span military, space exploration, scientific research, and hobbyist activities, making them one of the most versatile and widely used propellants in the aerospace industry. CSP consists of a mixture of a metal fuel and an oxidiser called Ammonium perchlorate (AP) bound together by a polymer binder, usually Hydroxyl-terminated polybutadiene (HTPB). Fundamentally, AP-based CSP has a very high combustion performance compared to other types of rocket fuel. However, AP-based CSP resulted in some drawbacks, which come from the emission of HCl gases as a combustion by-product. This HCl gas is a toxic gas and can affect a few environmental concerns: (i) ground-based impacts ranging from groundwater contamination to accidents caused by improper propellant processing and handling, (ii) atmospheric impacts resulting from the interaction of exhaust combustion products with the

surrounding atmosphere, including the ozone layer, and (iii) biological impacts encompassing propellant toxicity and corrosiveness. The main objective of this research is to synthesise and evaluate KMnO_4/AP dual oxidisers that reduce HCl concentration as combustion by-products in AP-based CSP. Potassium permanganate (KMnO_4) is a high oxidising agent and was introduced to minimise the usage of AP, which acts as KMnO_4/AP dual oxidiser. Incorporating KMnO_4 in a specific ratio will reduce the formation of HCl as a combustion by-product of CSP. KMnO_4 and AP were synthesised using the agate mortar mixing method and characterised in terms of morphological, elemental composition, crystallinity, molecular interaction, surface area, and thermal properties. Then, KMnO_4/AP was incorporated into the CSP system, and four experiments were conducted, which were the HCl concentration test, uniaxial tensile test and burn rate test. The HCl concentration test was evaluated using Mohr's titration method. Then, the tensile strength was tested using a uniaxial tensile test, and the burn rate was analysed using the Crawford burn rate. Factorial design (FD) and response surface methodology (RSM) were used to design the experiments incorporating three factors, namely ratio of KMnO_4 to AP, temperature, and pressure. These were developed to illustrate the relationship between those factors. From the findings, the sample of KMnO_4 (40:60) CSP exhibits 39.04% reduction percentage of chlorine content from the conventional AP CSP. In addition, the tensile strength properties of sample KMnO_4/AP (40:60) observed a value of 2.51 MPa at a temperature of 20 °C. Besides, the burn rate value resulted in an increase in value with increased pressure. KMnO_4/AP (40:60) CSP sample resulted in the highest burn rate value of 7.53 mm/s at 3 atm. This percentage

of chlorine content reduction could result in cleaner exhaust emissions, improving air quality and minimising biological health damage caused by HCl acidic by-products. Thus, incorporating KMnO_4 as a dual oxidiser with AP proved to be a promising candidate for developing environmentally friendly rocket fuel applications without compromising the combustion and mechanical performances.

Keywords: Solid Rocket Propellant, Oxidiser, Hydrogen Chloride Gases, Ammonium Perchlorate, Burn rate

SDG: GOAL 7: Affordable and Clean Energy, GOAL 9: Industry, Innovation, and Infrastructure, GOAL 13: Climate Action

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**DUAL OKSIDISER AP/ KMnO_4 MENGENAI PENGURANGAN GAS HCl
DAN PENINGKATAN SIFAT PEMBAKARAN BAGI PROPELLANT ROKET
PEPEJAL KOMPOSIT**

Oleh

IZZAT NAJMI BIN MOHD YAACOB

Januari 2025

Pengerusi : Norkhairunnisa binti Mazlan, PhD

Fakulti : Kejuruteraan

Propelan pepejal komposit (CSP) adalah penting kepada teknologi roket dan peluru berpandu moden kerana prestasi tinggi, kebolehpercayaan dan kemudahan penggunaannya. Aplikasi mereka merangkumi aktiviti ketenteraan, penerokaan angkasa lepas, penyelidikan saintifik dan hobi, menjadikannya salah satu jenis propelan yang paling serba boleh dan digunakan secara meluas dalam industri aeroangkasa. CSP terdiri daripada campuran bahan api logam dan pengoksida yang dipanggil Ammonium Perchlorate (AP) yang diikat bersama oleh pengikat polimer biasanya Hydroxyl terminated polybutadiena (HTPB). Pada asasnya, CSP berasaskan AP mempunyai prestasi pembakaran yang sangat tinggi berbanding jenis bahan api roket yang lain. Walau bagaimanapun, CSP berasaskan AP menyebabkan beberapa kelemahan yang datang daripada pelepasan gas HCl sebagai hasil pembakaran. Gas HCl ini adalah gas toksik dan boleh menjejaskan beberapa keseimbangan alam sekitar: (i) kesan berasaskan tanah

yang terdiri daripada pencemaran air bawah tanah kepada kemalangan yang disebabkan oleh pemprosesan dan pengendalian propelan yang tidak betul, (ii) kesan atmosfera yang terhasil daripada interaksi produk pembakaran ekzos dengan atmosfera sekeliling, termasuk lapisan ozon, dan (iii) impak biologi yang merangkumi ketoksikan propelan dan kekakisan. Objektif utama penyelidikan ini adalah untuk mensintesis dan menilai pengoksidaan dwi KMnO_4/AP yang mengurangkan kepekatan HCl sebagai hasil pembakaran dalam CSP berasaskan AP. Kalium permanganat (KMnO_4) adalah agen pengoksidaan tinggi dan diperkenalkan untuk meminimumkan penggunaan AP yang bertindak sebagai pengoksida dwi KMnO_4/AP . Penggabungan KMnO_4 ini dalam nisbah tertentu akan mengurangkan pembentukan HCl sebagai pembakaran oleh produk CSP. KMnO_4 dan AP disintesis menggunakan kaedah bancuhan mortar batu akik dan dicirikan dari segi morfologi, komposisi unsur, kehabluran, interaksi molekul, luas permukaan dan sifat terma. Kemudian, KMnO_4/AP telah dimasukkan ke dalam sistem CSP, dan empat eksperimen telah dijalankan iaitu ujian kepekatan HCl , ujian tegangan uniaxial dan ujian kadar terbakar. Ujian kepekatan HCl dinilai melalui kaedah pentitratan Mohr, kekuatan tegangan diuji menggunakan ujian tegangan uniaxial, dan kadar lecuran dianalisis menggunakan jenis kadar lecuran Crawford. Reka bentuk faktorial (FD) dan metodologi permukaan tindak balas (RSM) digunakan untuk mereka bentuk eksperimen yang menggabungkan tiga faktor; iaitu nisbah KMnO_4 kepada AP, suhu, dan tekanan dan kontur dan plot permukaan telah dibangunkan untuk menggambarkan hubungan antara faktor tersebut. Daripada penemuan, sampel KMnO_4 (40:60) CSP mempamerkan peratusan pengurangan

kandungan klorin sebanyak 39.04% daripada AP CSP konvensional. Di samping itu, sifat kekuatan tegangan sampel KMnO_4/AP (40:60) memerhatikan nilai 2.51 MPa pada suhu 20 °C. Selain itu, nilai kadar pembakaran menghasilkan peningkatan nilai dengan peningkatan tekanan. Sampel CSP KMnO_4/AP (40:60) menghasilkan nilai kadar pembakaran tertinggi iaitu 7.53 mm/s pada 3 atm. Peratusan pengurangan kandungan klorin ini boleh menghasilkan pelepasan ekzos yang lebih bersih, meningkatkan kualiti udara dan meminimumkan kerosakan kesihatan biologi yang disebabkan oleh produk sampingan berasid HCl. Oleh itu, penggabungan KMnO_4 sebagai pengoksida dwi dengan AP terbukti menjadi calon yang menjanjikan dalam pembangunan aplikasi bahan api roket mesra alam tanpa menjejaskan prestasi pembakaran dan mekanikal.

Kata Kunci: Propelan Roket Pepejal, Pengoksida, Gas Hidrogen Klorida, Ammonium Perklorat, Kadar Pembakaran

SDG: MATLAMAT 7: Tenaga Berpatutan dan Bersih, MATLAMAT 9: Industri, Inovasi, dan Prasarana, MATLAMAT 13: Tindakan Iklim

ACKNOWLEDGEMENTS

All praise is to Almighty Allah for His endless blessings, kindness, guidance, strength, and will, which motivated me to complete my doctoral study successfully. May His name be glorified and praised.

First and foremost, I would like to express my sincere appreciation and utmost gratitude to my supervisor, Associate Professor Dr Norkhairunnisa Mazlan, for her continuous support and invaluable guidance for my PhD study, for his patience, motivation, and enthusiasm. I want to extend my sincere appreciation to my excellent Supervisory Committee, Professor Ir. Dr. Kamarul Arifin Ahmad, Dr. Adi Azrif and Dr. Ezanee Gires to whom I owe an immense debt. During my doctoral study, they provided valuable advice, good tutoring, enlightening experiences, and the necessary facilities that generally kept me on track and focused throughout. Indeed, I could not wish for a better Supervisory Committee, and I am grateful for their strong supervision, which enabled me to complete this thesis.

I am grateful to all the lecturers and staff of the engineering faculty, ION2, STRIDE, and LESTARI AERO Industry, for facilitating me during my entire study period. Special thanks are credited to Mrs Afiza Saleh, Mrs Suraya Sahedi, Mr Osmera Ismail, Mr Fikri Rasih, Mrs Maisarah, Mr Rashidi, Mrs Suraya, Mr Johari, Mr Dato Azaddin and others whose names are not mentioned, for their kind and helpful assistance in laboratory analysis and for their valuable effort and time. May Allah bless their kind contribution. I am pleased to acknowledge Universiti Putra Malaysia for funding my study under

the Tenaga Akademi Muda (TAM) and Geran Putra IPS. I am also grateful to the SGS Conference Support Group Team, UPM, for their financial support.

I respectfully acknowledge the blessings and good wishes of all my dearest friends for their help, encouragement, and support. Special thanks to my dearest father, Mohd Yaacob bin Abdul Manaf; my beloved mother, Hanam binti Musa; my sisters, and brothers for their endless love, great sacrifice, patience, and support during my study. Finally, I want to express my gratitude to my friend Nurul Izzati binti Norsapei for supporting me in completing this journey.

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Norkhairunnisa binti Mazlan, PhD

Associate Professor. Ts
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Kamarul Arifin bin Ahmad, PhD

Professor. Ir
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Ezanee Gires, PhD

Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Adi Azriff bin Basri, PhD

Senior Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)

ZALILAH MOHD SHARIFF, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 17 April 2025

TABLE OF CONTENTS

ABSTRACT	Page
ABSTRAK	i
ACKNOWLEDGEMENTS	iv
APPROVAL	vii
DECLARATION	ix
LIST OF TABLES	xi
LIST OF FIGURES	xixi
LIST OF ABBREVIATIONS	xxii
LIST OF SYMBOLS	xxvii
CHAPTER	
1 INTRODUCTION	1
1.1 Research Background	1
1.2 Problem Statement	7
1.3 Research Objective	8
1.4 Scope and Limitation of The Study	9
1.5 Thesis Layout	11
1.6 Significant of The Study	12
2 LITERATURE REVIEW	13
2.1 Overview	13
2.2 Rocket propellant and The Classifications	13
2.2.1 Liquid Rocket Propellant	20
2.2.2 Solid Rocket Propellant	23
2.2.3 Hybrid Rocket Propellant	27
2.3 Solid Propellant Rockets (SPRs) Motor	29
2.4 Composite Solid Propellant (CSP) in Solid Propellant Rocket Motor Applications	31
2.4.1 Composite Solid Propellant (CSP) Composition and Formulation	32
2.4.2 Type of Oxidiser Used in Solid Propellant Rocket Applications	38
2.4.3 Aluminium as Metal Fuel in Composite Solid Propellant (CSP)	41
2.4.4 Hydroxyl-Terminated Polybutadiene (HTPB) Polymer Binder as A Composite Matrix in Composite Solid Propellant (CSP)	41
2.4.5 Additive Materials in Composite Solid Propellant (CSP) Application	42
2.5 Ammonium Perchlorate (AP) as A Primary Oxidiser in Solid Propellant Rocket Applications	46
2.5.1 Physical and Chemical Properties of Ammonium Perchlorate	47

2.5.2	Thermal Decomposition Properties of Ammonium Perchlorate as An Oxidiser in Composite Solid Propellant (CSP)	49
2.5.3	Thermal Decomposition Principle of Ammonium Perchlorate in Composite Solid Propellant (CSP) Combustion Process	52
2.5.3.1	Electron Transfer Principle in The Thermal Decomposition of Ammonium Perchlorate	54
2.5.3.2	Proton Transfer Principle in The Thermal Decomposition of Ammonium Perchlorate	55
2.5.4	Combustion By-Products of Ammonium Perchlorate in Solid Propellant Rockets Combustion Process	56
2.6	Potassium Permanganate (KMnO_4) as A Strong Oxidising Agent in Dual Oxidiser System of AP-Based CSP	58
2.6.1	Physical and Chemical Properties of Potassium Permanganate	58
2.6.2	Thermal Decomposition Properties of Potassium Permanganate	60
2.6.3	Combustion Product of KMnO_4 as Propellant Oxidiser	63
2.7	Hydrochloric Acid Gas (HCl) as Combustion By-Products of AP-Based CSP and its Effect on The Environment	66
2.7.1	Limiting Allowable Concentration of Hydrochloric (HCl) Gas in Environmental Aspect Condition	68
2.8	Hydrochloric (HCl) Gas Reduction Efforts in AP-Based Composite Solid Propellant Combustion By-Products	70
2.9	Tensile Properties and Behaviour of AP-Based Composite Solid Propellant Grain	77
2.9.1	Tensile Fracture Behaviour of Composite Solid Propellant Grain	80
2.10	Burn Rate Properties of AP-Based Composite Solid Propellants in The Combustion Process	85
2.11	Burn Rate Behavior Effect on The Performance of The Solid Rocket Motor	90
2.12	Combustion Mechanism Process of AP/HTPB-Based Composite Solid Propellant	92
2.13	Statistical Design of Experimental Methodology	97
2.13.1	Response Surface Methodology (RSM) in Design of Experiment (DOE) Approach	98
2.13.2	Factorial Design (FD) Approach	99
2.14	Summary	101

3	METHODOLOGY	103
3.1	Overview	103
3.2	General Method of Approach	103
3.3	Materials Sample Preparation for Experimental Works	105
3.3.1	KMnO ₄ /AP Synthesis Process and Sample Size	105
3.3.2	AP-Based Composite Solid Propellant Sample Fabrication Process	107
3.4	Characterization of KMnO ₄ /AP Dual Oxidiser and Composite Solid Propellant (CSP) Samples	112
3.4.1	Morphological Analysis	112
3.4.2	Thermal Analysis	113
3.4.3	Crystallinity Structure Properties	114
3.4.4	Surface Area Analysis	116
3.4.5	Molecular Interaction Analysis	117
3.4.6	Heat of Combustion Analysis	117
3.5	Experimental Testing and Analysis Procedure	119
3.5.1	Hydrochloric Acid (HCl) Gases Concentration in Combustion By-Product of Composite Solid Propellant (CSP) Samples Test	119
3.5.2	Uniaxial Tensile Test of Composite Solid Propellant (CSP) Grain	124
3.5.3	Burn Rate Analysis of Composite Solid Propellant (CSP) Sample	127
3.6	Design of Experimental (DOE) and Analysis Steps	131
3.6.1	Factorial Design (FD) Method Approach in The Research Work	132
3.6.1.1	Factorial Design (FD) Method for Uniaxial Tensile Test and Analysis	136
3.6.1.2	Factorial Design (FD) Method for Burn Rate Test and Analysis	137
3.6.2	Response Surface Methodology (RSM) as Experimental Analysis Modelling	138
3.6.2.1	Response Surface Methodology (RSM) for Uniaxial Tensile Test and Analysis	141
3.6.2.2	Response Surface Methodology (RSM) for Burn Rate Test and Analysis	142
3.7	Summary	142
4	RESULTS AND DISCUSSION	144
4.1	Overview	144
4.2	Dual Oxidiser KMnO ₄ /AP Characterizations	145
4.2.1	Physical Observation of AP, KMnO ₄ , and Dual Oxidiser KMnO ₄ /AP	145
4.2.2	Morphological Analysis of AP, KMnO ₄ , and Dual Oxidiser KMnO ₄ /AP	147

4.2.3	Elemental Composition Analysis of AP, KMnO ₄ , and Dual Oxidiser KMnO ₄ /AP	150
4.2.4	Crystallinity Properties Analysis (XRD) of AP, KMnO ₄ , and Dual Oxidiser KMnO ₄ /AP	154
4.2.5	Molecular Structure and Interaction Analysis of AP, KMnO ₄ , and Dual Oxidiser KMnO ₄ /AP	159
4.2.6	Surface Area Analysis of AP, KMnO ₄ , and Dual Oxidiser KMnO ₄ /AP	162
4.3	Catalytic Behavior of AP, KMnO ₄ , and Dual Oxidiser KMnO ₄ /AP	167
4.3.1	Thermal Decomposition Temperature of AP, KMnO ₄ , and Dual Oxidiser KMnO ₄ /AP	167
4.4	Characterization of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	173
4.4.1	Physical Characteristics of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	173
4.4.2	Morphological Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	175
4.4.3	Elemental Composition Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	178
4.4.4	Thermal Decomposition Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	182
4.5	Heat of Combustion Analysis Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	191
4.5.1	Energetic Properties (Density and Heat of Combustion) of Composite Solid Propellant (CSP) with A Dual Oxidiser (KMnO ₄ /AP) Based	191
4.6	HCl Concentration Analysis in Combustion Product of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	193
4.6.1	HCl Concentration Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	193
4.7	Uniaxial Properties Testing Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based	199
4.7.1	Stress-Strain behaviour of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based Sample	199

4.7.2	Factorial Design in RSM of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based Sample	206
4.7.2.1	Statistical Analysis in Uniaxial Tensile Properties Testing	207
4.7.2.2	Regression Model of Uniaxial Tensile Properties Testing	208
4.7.2.3	Pareto Plot of Uniaxial Tensile Properties Testing	208
4.7.2.4	Normal Probability Plot of Residual in Uniaxial Tensile Properties Testing	209
4.7.3	Response Surface Methodology (RSM) of Uniaxial Tensile Properties Testing	210
4.7.3.1	Effect of Factors on Tensile Strength, Maximum Elongation, and Young's Modulus Properties	211
4.7.4	Summary	217
4.8	Burn Rate Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based Sample	218
4.8.1	Factorial Design in RSM of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO ₄ /AP) Based Sample	218
4.8.1.1	Statistical Analysis in Burn Rate Test	218
4.8.1.2	Regression Model of Burn Rate Test	219
4.8.1.3	Pareto Plot of Burn Rate Test	220
4.8.1.4	Normal Probability Plot of Residual of Burn Rate Test	220
4.8.2	Response Surface Methodology (RSM) of Burn Rate Test	221
4.8.2.1	Effect of Factors on Burn Rate Characteristics of CSP Samples	222
4.8.3	Effect of Burn Rate on The Mass Flow Rate of The CSP for Solid Rocket Motor Applications Performances.	227
4.8.4	Summary	228
5	SUMMARY, CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH	231
5.1	Conclusion	231
5.2	Main Contributions	238
5.3	Recommendations for Future Research	239
	REFERENCES	240

APPENDICES	265
BIODATA OF STUDENT	295
LIST OF PUBLICATIONS	296

265
295
296



LIST OF TABLES

Table	Page
2.1 Liquid propellant standard composition and their properties	22
2.2 Solid and liquid propellant comparison	26
2.3 Comparison between solid and hybrid rocket propellant	28
2.4 Solid propellant formulation characteristics	34
2.5 Common materials and chemicals for composite solid propellant (CSP)	36
2.6 Common crystalline oxidisers and their properties used in AP-based solid propellant rockets	40
2.7 Chemical Structure of Isodecyl Pelargonate (IDP) and Dibutyl Adipate (DOA)	43
2.8 Chemical properties of Ammonium Perchlorate (AP)	49
2.9 Chemical properties of Potassium Permanganate (KMnO_4)	59
2.10 Physical and chemical properties of hydrochloric acid (HCl)	67
2.11 Acute exposure guideline level (AEGl) value for hydrochloric acid gas (HCl) ($\text{ppm} [\text{mg}/\text{m}^3]$)	69
2.12 Effects of hydrogen chloride (HCl) concentration on human respiratory health	69
2.13 Tensile mode theoretical parameter constraints for composite solid propellant	82
2.14 Critical analysis on mitigating HCl gases efforts as combustion by-products of CSP	102
3.1 Sample size and the chemical composition of KMnO_4/AP dual oxidiser	107
3.2 Composition and formulation of composite solid propellant (CSP) samples (a) AP-based CSP, (b) KMnO_4/AP (20:80) based CSP, (c) KMnO_4/AP (40:60) based CSP, KMnO_4/AP (60:40) based CSP, KMnO_4/AP (80:20) based CSP	110
3.3 Coded and uncoded factor values of uniaxial tensile test	136
3.4 Coded and uncoded factor values of burn rate test	137

3.5	Comparison of the total number of experiments run between the conventional method and RSM	139
3.6	Factors and levels used for uniaxial tensile test	142
3.7	Factors and levels used for burn rate test	142
4.1	Elemental composition percentage of all the samples from EDX result analysis	153
4.2	Crystallinity dimensions of AP, KMnO_4 , and KMnO_4/AP with different KMnO_4 to AP ratios	157
4.3	BET surface area, pore sizes, and pore volume distribution of the AP, KMnO_4 and KMnO_4/AP with different ratios	166
4.4	Low-temperature decomposition (LTD), high-temperature decomposition (HTD) and heat release (ΔH) results of all the samples in this study	172
4.5	Thermal decomposition performance of AP in this work compared with the literature	173
4.6	EDX result analysis of CSP with single oxidiser AP and dual oxidiser KMnO_4/AP	181
4.7	Low-temperature decomposition (LTD), high-temperature decomposition (HTD) and heat release (ΔH) result of AP and KMnO_4/AP -based CSP with different ratios	189
4.8	Effects of KMnO_4 with different ratios on the energetic properties of AP-based CSP	192
4.9	Result of chlorine content from the Mohr's titration method	196
4.10	Percentage reduction from the pure AP CSP	197
4.11	Sample comparison of stress and maximum elongation value of CSP samples at different temperatures and KMnO_4 to AP ratio	204
4.12	Estimated effects and coefficient for tensile strength	207
4.13	Design matrix and response values for uniaxial tensile test	211
4.14	Estimated effects and coefficient for burn rate test	219
4.15	Design matrix and response values for burn rate test	222
4.16	Burn rate result data of CSP samples with various pressures	224

4.17	Burn rate result validation with other studies in the development of dual oxidiser	226
4.18	Mass flow rate value for all the CSP samples used in this research study	227



LIST OF FIGURES

Figure		Page
2.1	Rocket propulsion systems (a) liquid-propellant rocket engine, (b) Solid-propellant rocket motor, and (c) Hybrid-propellant rocket motor	16
2.2	Rocket propellant motors classification	20
2.3	Solid rocket propellant classification	25
2.4	Typical solid propellant rocket motor design	30
2.5	Common types of additives used in composite solid propellant rockets	45
2.6	Ammonium perchlorate (AP) as a white, odourless crystal	48
2.7	Typical (a) Differential scanning calorimetry (DSC) and (b) Thermogravimetric analysis (TGA) curve of ammonium perchlorate (AP)	51
2.8	Ammonium perchlorate (AP) and its combustion products affect the environment	57
2.9	Physical structure of potassium permanganate (KMnO_4)	58
2.10	Application of potassium permanganate (KMnO_4)	60
2.11	Thermal properties of potassium permanganate (KMnO_4) using (a) thermogravimetric analysis (TGA) under nitrogen atmosphere, (b) differential scanning calorimetry (DSC) under nitrogen atmosphere	62
2.12	Hypothesis of KMnO_4/AP composite solid propellant effect on the combustion by-products in solid rocket motor application	65
2.13	Research finding on the current developed promising materials for replacing ammonium perchlorate (AP) as composite solid propellant (CSP) oxidiser and additives in reducing HCl as combustion by-products with their burn rate performance	72
2.14	Efforts on HCl reduction of AP-based CSP based on literature findings	76

2.15	Stress-strain curves of composite solid propellants subjected to various loading conditions (a) Uniaxial compression, (b) Low-temperature quasi-static compression, (c) High-strain-rate compression, and (d) Low-temperature quasi-static uniaxial tension	83
2.16	Burning surface regression of the composite solid propellant grain	86
2.17	Crawford strand burner setup schematic diagram for burn rate testing	88
2.18	Vieille's Law may describe a typical propellant's burn rate and pressure dependency, which produces a straight line on a log-log diagram.	90
2.19	Effect of mass flow rate value on the thrust performance of the solid propellant rocket	92
2.20	Overview of combustion mechanism process in AP/HTPB composite solid propellant	95
3.1	Flow chart of overall research study	103
3.2	Flow chart of KMnO_4 /AP synthesis process	104
3.3	Synthesis process of KMnO_4 /AP using agate mortar pestle (a) Weigh (b) Mix with ethanol (c) Mix KMnO_4 with AP (d) Mix and crushing using agate mortar and pestle (e) Vacuum filtration and (f) Drying	106
3.4	Flow chart of composite solid propellant sample fabrication process	108
3.5	Materials and chemicals preparation in composite solid propellant fabrication process flow chart	109
3.6	Fabrication process of composite solid propellant (a) weighting, (b) sieving, (c) mixing, (d) casting, (e) curing, and (f) cured samples	112
3.7	Bomb calorimetry (a) schematic diagram setup and (b) propellant setup in a crucible of bomb calorimetry	118
3.8	Schematic diagram of (a) gas bubbling setup and (b) Mohr's method on titration of HCl gases	120
3.9	(a) CSP sample with visco fuse wire and (b) 6mm x 6mm x 100mm propellant sample	121

3.10	Experimental setup of (a) Gas bubbling setup and (b) Mohr's titration	122
3.11	Color references of (a) water sample (b) midpoint titration, and (c) end-point titration	123
3.12	Test set-up for (a) the uniaxial tensile test and (b) the environmental chamber	125
3.13	Propellant dog bone sample according to JANNAF standard specimens	126
3.14	Sample preparation setup on tensile testing machine (a) sample clamping and (b) strain gauge attachment to the dog bone propellant samples	127
3.15	Crawford type strand burner setup (a) close-up view on pressure gauge and sample holder setting and (b) full view	128
3.16	Propellant strands samples for burn rate test of composite solid propellant	129
3.17	Propellant strand sample attached to the sample holder	130
3.18	Overall flowchart process of factorial design	133
3.19	Flow chart of RSM used in this study	140
4.1	Physical condition of the sample of AP and KMnO_4 and KMnO_4/AP dual oxidiser with different AP to KMnO_4/AP ratios	146
4.2	FESEM morphology of (a) AP, (b) KMnO_4 , (c) KMnO_4/AP (20:80), (d) KMnO_4/AP (40:60), (e) KMnO_4/AP (60:40), and (f) KMnO_4/AP (80:20) after dry for 1 hour	148
4.3	EDX and mapping of (a) AP and (b) KMnO_4	151
4.4	EDX and mapping of (a) KMnO_4/AP (20:80) (b) KMnO_4/AP (40:60) (c) KMnO_4/AP (60:40) and (d) KMnO_4/AP (80:20)	152
4.5	Crystallinity plot in XRD analysis of AP, KMnO_4 , KMnO_4/AP (20:80), KMnO_4/AP (40:60), KMnO_4/AP (60:40), and KMnO_4/AP (80:20)	156
4.6	Raman spectrum of AP, KMnO_4 , and KMnO_4/AP with various KMnO_4 to AP ratios	160

4.7	N ₂ adsorption–desorption isotherms of (a) AP, (b) KMnO ₄ , and (c) KMnO ₄ /AP with different KMnO ₄ to AP ratios	163
4.8	Pore volume and size distributions of (a) AP, (b) KMnO ₄ , and (c) KMnO ₄ /AP with different KMnO ₄ to AP ratio	165
4.9	TGA and DSC result of the sample (a) AP and (b) KMnO ₄	168
4.10	Analysis result of (a) TGA and (b) DSC of KMnO ₄ /AP samples with different ratios	169
4.11	Physical condition of (a) AP CSP, (b) KMnO ₄ /AP (20:80) CSP, KMnO ₄ /AP (40:60) CSP, KMnO ₄ /AP (60:40) CSP, KMnO ₄ /AP (80:20) CSP	174
4.12	SEM image of composite solid propellant samples of (a) AP, (b) KMnO ₄ /AP (20:80), (c) KMnO ₄ /AP (40:60), (d) KMnO ₄ /AP (60:40), and (e) KMnO ₄ /AP (80:20) based	176
4.13	EDX mapping of (a) AP-based CSP (b) KMnO ₄ /AP (20:80) based CSP (c) KMnO ₄ /AP (40:60) based CSP (d) KMnO ₄ /AP (60:40) based CSP, and (e) KMnO ₄ /AP (80:20) based composite solid propellant	179
4.14	TGA and DSC result of samples AP-based CSP	183
4.15	TGA plotting results of samples AP and KMnO ₄ /AP with different ratios based on CSP	185
4.16	DSC plotting results of samples AP and KMnO ₄ /AP with different ratios based on CSP	188
4.17	The result of the water sample at (a) initial, (b) Mid, (c) end point of Mohr's titration	193
4.18	Bar chart comparison result of CSP samples chlorine concentration value in experimental work with literature	198
4.19	Stress-strain behaviour of CSP samples (a) AP, (b) KMnO ₄ /AP (20:80), (c) KMnO ₄ /AP (40:60), (d) KMnO ₄ /AP (60:40), (d) KMnO ₄ /AP (80:20) at different temperatures	200
4.20	Physical state of dog bone samples after uniaxial tensile test	205
4.21	Pareto plot of the standardised effects on tensile strength	209
4.22	Normal probability plot of the residual data for tensile strength	210

4.23	Contour plot for the effect of the ratio of KMnO_4 to AP and temperature on the tensile strength properties of CSP	212
4.24	Contour plot for the KMnO_4 to AP ratio and temperature on the maximum strain of CSP samples	213
4.25	Surface plot of KMnO_4 to AP ratio and temperature for the maximum strain value	214
4.26	Contour plot for the KMnO_4 to AP ratio and temperature on Young's Modulus	215
4.27	Surface plot of temperature and KMnO_4 to AP ratio for Young's modulus	216
4.28	Pareto plot of the standardized effects on burn rate test	220
4.29	Normal Probability plot of the residual data for burn rate test	221
4.30	Contour plot for the effect of the ratio of KMnO_4 to AP and pressures on the burn rate characteristics of CSP samples	223
4.31	Surface plot for the effect of the ratio of KMnO_4 to AP and pressures on the burn rate characteristics of CSP samples	225

LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
ADN	Ammonium Dinitramide
AEGL	Acute Exposure Guideline Level
Al	Aluminium
Al ₂ O ₃	Aluminium oxide
AN	Ammonium Nitrate
AP	Ammonium Perchlorate
APCP	Ammonium Perchlorate Composite Propellants
ATK	Alliant Techsystems
Ag	Silver
AgCl	Silver Chloride
AgNO ₃	Silver Nitrate
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BAMO	3,3-Bis(azidomethyl)Oxetane
BET	Brunauer-Emmett-Teller
BITA	Trimesoyl- 1 (2-ethyl)-Aziridine
BTTN	Butanetriol trinitrate
C	Carbon
CAS	Chemical Abstracts Service
CCD	Central Composite Design
CIO	Chloroxide
CMDB	Composite Modified Double Base

CNT	Carbon Nanotube
CO ₂	Carbon Dioxide
CPS	Chlorinated Paraffins
CTPB	N-(4-chloro-3-trifluoromethyl-phenyl)-2-methoxy-6-pentadecyl-benzamide
CuO	Copper Oxide
CrO ₄	Chromate
DB	Double Based
DBP	Dibutyl Phthalate
DBS	dibutyl Sebacate
DDI	Dimeryl Diisocyanate
DEGDN	Diethylene Glycol Dinitrate
DEP	Diethyl Phthalate
DMP	Dimethyl Phthalate
DNB	Dinitrobenzene
DOA	Diethyl Adipate
DOE	Design of Experiment
DOP	Diethyl Phthalate
DOS	Diethyl Sebacate
DPA	Diphenylamine Phenyl naphthylamine
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-ray Spectroscopy
EEC	Estimated Effect and Coefficient
FD	Factorial Design
FeO	Ferric Oxide
FESEM	Field Emission Scanning Electron Microscope

FWHM	Full-Width At Half-Maximum
GAP	Glycidyl Azide Polymer
Ge	Graphene
GSLV	Geosynchronous Satellite Launch Vehicle
H ₂	Dihydrogen
H ₂ O	Water
HAN	Hydroxylammonium Nitrate
HCl	Hydrochloric Acid Gases
HMDI	Hexamethylene diisocyanate
HMX	Octogen
HNF	Hydrazinium nitroformate
HNIW	Hexanitrohexaazaisowurtzitane
HNO	Nitroxyl
HTD	High-Temperature Decompositions
HTPB	Hydroxyl Terminated Polybutadiene
HX-752	Acyl Aziridines
IDP	Isodecyl Pelargonate
IPDI	Isophorone Diisocyanate
I _{sp}	Specific Impulse
K	Potassium
K ₂ O	Potassium Oxide
KCl	Potassium Chloride
KMnO ₄	Potassium Permanganate
KNO ₃	Potassium Nitrate
LAC	Limits The Allowable Concentration

Li	Lithium
LOX	Liquid Oxygen
LTD	Low Temperature Decompositions
MAPO	Methyl Aziridiny Phosphine Oxide
MAPO	Tartaric Acid-Adipic Acid
ME	Error margin
Mg	Magnesium
MnO	Manganese Oxide
MOF	Metal-Organic Framework
N ₂	Nitrogen Gas
nBF	n-Butyl Ferrocene
NC	Nitrocellulose
NG	Nitroglycerin
NH ₄	Ammonium
NiO	Nickel Oxide
NMA	N-methyl-p-Nitroaniline Dinitrodiphenylamine
NMMO	Nitro Methyl methyl oxetane copolymer
NOEL	No Observed Effect Level
NPs	Nanoparticles
OH	Hydroxide
PBAA	Polybutadiene Acrylic Acid
PBAN	Polybutadiene Acrylonitrile
PCP	Polycaprolactone polyol
PEG	Polyethylene Glycol
PGA	Polyglycol Adipate

PGN	Propylglycidyl Nitrate
PPG	Polypropylene Glycol
PSAN	Phase-Stabilized Ammonium Nitrate
PSE	Pseudo-Standard Error
PU	Polyurethane Polyester
PVC	Polyvinyl Chloride
RAMAN	Raman Spectroscopy
RDX	Hexogen
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
SRMs	Solid Rocket Motors
SRPs	Solid Rocket Propellants
STP	Standard Temperature and Pressure
TDI	Toluene Diisocyanate
TEGDN	Triethylene Glycol Dinitrate
TMETN	Trimethylolethane Trinitrate
TMP	Trimethylolpropane
UTM	Universal Testing Machine
UTS	Ultimate Tensile Strength
XRD	X-ray Diffraction

LIST OF SYMBOLS

K	Kelvin
°C	Degree Celcius
°F	Fahrenheit
%	Percentage
cm	Centimetre
cm ³	Centimetre cube
µm	Micrometre
m	metre
ft	feet
s	second
M	Molar
MPa	Mega Pascal
V ₁	Factor 1
V ₂	Factor 2
C*	Characteristic velocity
V _e	Exhaust velocity
g	gram
kg	Kilogram
J	joule
ml	millilitre
rpm	Revolution per minute
lb	pound
in	inches
wt%	Weight percentage

psi	Pound per square inch
T_g	Glass transition temperature
h	hour
min	minute
atm	atmosphere
ppm	Parts per million
mg/m ³	Milligrams per Cubic Meter
σ	Maximum stress
ϵ	Strain
t	time
$\dot{r}$	Burn rate
P_c	Chamber pressure
$\dot{m}$	Mass flow rate
F	Thrust
P_e	Exhaust pressure
P_a	Ambient pressure
A_e	Area of the nozzle throat
ρ	Density
A	Burning surface area
g_0	Standard gravity acceleration
kV	Kilovoltage
λ	Wavelength
Å	Angstrom
θ	Theta
d	Lattice spacing

K	Scherrer constant
β	Full Width at Half-Maximum
P_o	Saturation pressure
V_m	Monolayer Volume of Gas Adsorbed
M_1	Molarity of $AgNO_3$
M_2	Molarity of the water sample
L_p	Propellant length
t_p	Propellant burning time
N	Number of experimental runs
L^k	Level of factors
$^\circ$	Degree
α	Alpha
β	Beta
γ	Gamma
Δ	Change in value
cal/g	Calorie per gram
R^2	Coefficient of determination

CHAPTER 1

INTRODUCTION

1.1 Research Background

Solid rocket motors (SRMs) are distinguished from other propulsion systems (such as nuclear, electric, and radiant) by using solidified mixtures of propellant components. These propellants discharge intensely heated gases at high velocities, propelling payloads ranging from satellites to warheads. While comprehensive overviews on the fundamentals and history of SRMs have been documented elsewhere, and the research and development of this technology is presently in progress. Solid propellants are utilised in numerous aircraft and rocket systems, including but not limited to intercontinental and submarine ballistic missiles, space launcher boosters, aeroplane ejection seats and amateur recreational rockets (Zeping et al., 2017). They are preferred over liquid and hybrid propellants due to their compactness, reliability, and availability of ready-to-use systems. Additionally, they have a lower cost of propulsion systems. Solid rocket propellants (SRPs) generally can be classified into two overarching categories which are homogeneous (double-base) propellants, which comprise a single molecule containing both the oxidiser and fuel, and heterogeneous (composite) propellants, composed of mechanical mixtures of distinct components (Dinesh et al., 2016). SRPs are a type of rocket propellant in which the fuel and oxidiser are mixed in a solid form. Unlike liquid rocket propellants, which are stored in separate tanks and mixed just before use, solid rocket propellants are preloaded into the rocket motor casing. The propellant is typically a mixture of a powdered fuel, an

oxidiser, a powdered metal or polymer binder, and other additives. These highly charged substances discharge their energy via gradual deflagration mechanisms, and complete combustion can span several seconds (Suksila et al., 2018). The performance of each propellant type in SRPs depends on the compositions and formulations. Besides, the choice of the wide variety of oxidiser constituents and their impact on the performance of composite solid propellant formulations and environmental considerations must be considered.

Fundamentally, composite solid propellant (CSP) is made up of solid fuel and oxidiser particles suspended in a polymeric matrix or binder, often aluminium (Al) and ammonium perchlorate (AP) (Vara et al., 2019). The CSP emit regulated amounts of energy and burns exclusively on exposed surfaces. The resulting combustion gases pressurise the rocket motor vessel. They create thrust by venting through a convergent and divergent nozzle design. On the regressing solid surface, the propellant is used until the entire mass is gone, which is called complete combustion (Gallier et al., 2016). The rate of charge, or grain, combustion gas generation is thus determined by the total exposed surface area during the burning process. Depending on the mission's requirements, this may be inconsistent. The history of burning surface area is determined by grain geometry. When burning occurs on the exposed fracture faces of grains with surface cracks, the combustion process may be disturbed (Wang et al., 2018). CSP and quality control development have been empirical trials and error-procedures. To compensate for the lack of detailed understanding of the degradation mechanisms, cautious rules are adopted in

propellant deployment. Several propellant formulations and batches were studied to get reliable batch-wise material data for failure prediction models.

Solid propellants are structural materials, and handling them presents difficult technological challenges, particularly in heavily loaded systems that include 85–90% solids and 10-15% liquid (Szala et al., 2020). Processing calls for in-depth knowledge of particle technology, rheology, propellant chemistry, manufacturing processes, and the safe handling of explosives and hazardous chemicals. Modern rocket motors must be built to withstand a wide range of mission applications, which places extreme requirements on the propellant grain's structural integrity (Demko et al., 2018). A propellant grain must withstand various loading conditions, including handling, vibration, ignition, pressurisation, and acceleration (Kebritchi et al., 2018). For the designer, quantitative measurements of the mechanical properties of the propellant are now crucial. Solid oxidiser, powdered metal, organic polymeric binder, plasticiser, curing agent, antioxidant, and burning rate catalyst are the usual components of a CSP used in SRPs. These chemicals are combined into a single, homogeneous mass in the form of propellant slurry. The propellant slurry will then be cast within an engine case and let to solidify, or it is moulded into a grain to be placed inside an engine. The conventional formulation weight percentage in CSP usually consists of 50-70% of oxidiser, 10-30% metal fuel, 0-15% polymer binder, 0-7% plasticiser, 0-3.5% curing agent, and 0-10% burn rate modifier (Gnanaprakash et al., 2018). Ammonium perchlorate (AP) is the most often utilised oxidiser since it meets most propellant needs. It has strong heat production, high oxygen content that is needed for the combustion

process, and a long shelf life (Lin et al., 2018). The most significant visible downside of AP is its chlorinated exhaust emissions, which are harmful to the environment and leave a recognisable trail behind missiles that can be easily traced.

AP has been an extensively used and proven oxidiser since it took the position of potassium perchlorate in the late 1940s (Liu et al., 2020). AP is a white, crystalline powder with a density of around 1949 kg/m³ at normal temperature. Like other perchlorates, AP has a strong oxidising ability and has been employed in pyrolants, which are materials that burn with intense heat, as well as propellants of different kinds (Hu et al., 2019). The stability of AP, which produces safe munitions, and its capacity to regulate a propellant's burning rate are two of the main factors contributing to its widespread use. The key benefits of AP-based propellants are high specific impulses, high dependability, and a straightforward production procedure (Zeng et al., 2019). Because of these performance characteristics, AP-based propellant is frequently employed in booster applications such as space exploration rockets, aircraft ejection, and international ballistic missiles. Furthermore, the presence of chlorine (Cl) elements in AP sets it apart from other explosive and propellant chemicals. The only elements found in most other energetic materials are carbon (C), hydrogen (H), nitrogen (N₂), and oxygen (O₂). Moreover, impurities significantly impact how quickly AP materials ignite, burn, and decompose in the combustion process. According to Yan et al. (2018), these difficulties have left the reaction chemistry of AP mostly unclear. The thermal decomposition properties of AP influence the propellant's combustion

behaviour because this is a crucial part of the mechanism of the CSP combustion process (Thomas et al., 2019).

Furthermore, the composite solid propellant formulations based on AP, which are currently the most used in conjunction with Hydroxyl Terminated Polybutadiene (HTPB), particularly for space exploration missions, have a negative impact on the environment and personal health due to the abundant of hydrochloric acid gases (HCl) emissions from the exhaust as combustion products (Biliaiev et al., 2019). Additional challenges emerge from the disposal of AP-based energetic materials for various military purposes. More broadly, the never-ending search for ever-better propelling systems leads to ever-higher performance levels in terms of specific impulse (I_{sp}) and density while keeping all environmental respect, storage, dangers, cost, processability, and mechanical qualities within reasonable bounds (Kuan et al., 2020). Particularly, the qualities of the new solid rocket formulations ought to be on par with or better than those of the existing AP/Al/HTPB-based arrangements. Furthermore, smokeless, low-signature, and ecologically friendly formulations are being explored for military uses (Dallas et al., 2020). In this regard, some rocket propellant laboratories are investigating a variety of novel substances as potential candidates for industrial applications. Although many high-energy density materials have been identified to overcome the shortcomings, most of them are far from being practicable in the short term due to a variety of severe difficulties in large-scale manufacture, ground processing, personnel safety at various stages, handling and transportation safety, shock sensitivity, prolonged storage, and cost considerations.

Potassium permanganate (KMnO_4) is a chemical compound consisting of potassium (K), manganese (Mn), and oxygen (O). It is a powerful oxidising agent with a distinctive purple colour. KMnO_4 is a strong oxidising agent because it readily donates oxygen atoms in redox reactions. The manganese element in potassium permanganate can exist in multiple oxidation states, including +7 in KMnO_4 (Rettinger et al., 2019). In this highly oxidised state, manganese can transfer electrons to other elements, resulting in their oxidation. This property makes it valuable in various applications, including water treatment, combustion process, chemical analysis, and redox titrations in laboratories (Papliński et al., 2019). Moreover, due to the uniqueness of KMnO_4 as an oxidising agent, it is proposed to be one of the promising oxidisers in rocket propellant. In this study, KMnO_4 is synthesised together with AP to produce a dual oxidiser for CSP. KMnO_4 is also proposed to be a catalyst in the decomposition process of AP. This will make the combustion process of CSP faster as the main phenomenon of propellant combustion is AP decomposition (Wang et al., 2019). Besides, incorporating KMnO_4 with AP suggests reducing the production of HCl as a toxic gas in combustion products. The chemical reaction of this KMnO_4 with AP in reducing HCl gases and the combustion mechanism will be discussed further in this research work.

The burning rate of the solid propellant is one of the most significant design parameters for rockets that use solid propellants. As a result, the burning rate of the propellant that will be employed in rocket motor design must first be determined. The propellant's regression perpendicularly from the nucleus's centre is used to express the burning rate of solid propellant (Varghese et al.,

2017). The combustion chamber pressure, the initial temperature of the solid propellant before ignition, the percentage of high-energy matters in the propellant content, the burn sensation of the flammable substance, the additional chemical substances regulating the burning rate, and the percentage of the amount of oxidising agent all influence the burning rate of solid propellants (Dey et al., 2015). In this study, the burn rate performance of CSP using novel oxidiser AP/KMnO₄ will be examined. This parameter is very important in developing an environmentally friendly propellant oxidiser without compromising the combustion performance.

1.2 Problem Statement

The use of ammonium perchlorate (AP) as an oxidiser in composite solid propellants (CSP) creates a serious challenge due to the combustion reaction that produces hydrochloric acid gases (HCl) as combustion products. In AP-based CSP, this potent oxidant makes up between 60 and 80 % of the total solid components. Furthermore, AP-based CSP produces roughly 98 % of the chlorine ions that are transformed into HCl gas (Terry et al., 2016). Ozone depletion, acid rain, climate change, and other negative consequences on human health are caused by the buildup of HCl in the atmosphere (Chalghoum et al., 2020). According to Wu et al. (2023), hydrogen chloride is bad for the environment and makes it easier to spot rocket launches since it causes white smoke to form behind the nozzle. Although many potential alternatives to AP have been identified, most of them are not yet practically employed in real applications due to a range of complex mixing processes, including high costs.

Numerous efforts have been made to develop formulations that remove or minimise the generation of HCl during combustion, and a great deal of studies have been focused on reducing the emissions of HCl from CSP combustion products. Although bimetal scavengers and highly energetic additives have been proposed as potential solutions, these strategies have been determined to be unfeasible because of the intricacy of their production processes and challenges in finding raw materials (Chalghoum et al., 2020; Gou et al., 2022). Due to this, much research has been done on finding eco-friendly oxidants that might be used to replace ammonium perchlorate (AP). However, it is not possible to totally replace AP because it meets the solid fuel oxidiser criteria of being oxygen content, able to burn well, and generally safe to handle (Gong et al., 2020; Gańczyk-Specjalska et al., 2021; Wen et al., 2021).

Consequently, it is essential to develop an eco-friendly oxidiser to mitigate HCl emissions from rocket exhaust. The dual new oxidiser AP/KMnO₄ proposed herein functions as both an oxidant and a combustion catalyst, as KMO₄ reduces the decomposition temperature of AP and diminishes smoke production. Consequently, reduced HCl production renders it an exemplary choice for environmentally beneficial practices. This research aims to design and formulate a novel AP/KMnO₄ composite solid propellant (CSP) to minimise the emission of HCl gas without sacrificing combustion performance.

1.3 Research Objective

This research aims to synthesise, characterise, and analyse the novel dual oxidiser ammonium perchlorate/potassium permanganate (AP/KMnO₄) in

terms of hydrochloric acid gases (HCl) production as combustion products and combustion behaviour in AP-based composite propellant. In addition to the primary objective, there are other distinct objectives, which include:

- I. To synthesise AP/KMnO₄ as a novel dual oxidiser, characterise its morphology and physical properties, and elucidate its catalytic behaviour by assessing the influence of KMnO₄ on the thermal decomposition temperature of AP.
- II. To investigate and compare the chlorine concentration value (in ppm) as combustion by-products of AP/KMnO₄ based with the conventional AP-based solid propellant.
- III. To assess the impact of using AP/KMnO₄ as a dual oxidiser on the tensile strength of AP-based composite solid propellants under various temperature conditions, employing response surface methodology for a comprehensive analysis.
- IV. To analyse and validate the effect of AP/KMnO₄ as a dual oxidiser on the burn rate behaviour of AP-based composite solid propellant in various pressure conditions using response surface methodology.

1.4 Scope and Limitation of The Study

To achieve the objective of this research study, experimental tests were carried out to assess HCl concentration, mechanical properties, heat of combustion, and burn rate characteristics of the propellant. These tests focused on three key features: chemical, thermal, and mechanical. Three factors were considered: (i) Ratio of KMnO₄ to AP, combustion chamber

pressure, strain rate, and environmental chamber temperature. AP was utilised as the main oxidiser, while sodium KMnO_4 was employed as an additional oxidiser that combined with AP to make a novel oxidiser. Five types of composite solid propellant formulations were designed and fabricated according to the stoichiometric condition of the composition. All the samples were prepared using different designs and dimensions due to the standard testing sample specification for each test. Statistical techniques for the design of the experiment, such as fractional factorial design and response surface methodology (RSM), were used for experimental design and analysis. The dual oxidiser samples underwent six characterisations, including physical, morphological, elemental composition, crystallinity, molecular interaction, and thermal properties. In contrast, CSP samples underwent three tests: chlorine concentration test, uniaxial test, and burn rate test.

This CSP study does not focus on curing and polymer chain properties, as they are beyond the scope of this research. Besides, the propellant sensitivity is also not covered in this thesis as these properties are focusing on the flash point of the propellant sample. In addition, the thrust performance of the CSP sample in the rocket motor chamber also will not be covered in this research work. This is because both sensitivity sample test and thrust performance of the propellant test are categorised in the application evaluation of the solid rocket propellant research and development. In this research work, the fundamental characterisation of novel materials and samples will be evaluated first, and the assessment of the combustion performance as well as the focus scope, which is chlorine concentration reduction, will be done.

1.5 Thesis Layout

The thesis consists of five chapters, and each chapter contains a subchapter according to the specific topics and explanations. The first chapter introduces the brief background of the composite solid propellant (CSP), the problem statement, the objectives of this study, the scope of the study and the thesis layout. The second chapter reviews the current issues in CSP and classifies the type of solid rocket propellant (SRP) type used in this research. It presents a literature review of CSP combustion mechanisms, combustion products, catalytic performances of current promising materials, mechanical properties, and burn rate behaviour. Moreover, this chapter only collects data from previous studies on developing dual oxidisers as environmentally friendly CSP formulations. Chapter 3 describes the materials and methodology used in this study. It focuses on a specific approach in designing and planning the course of study, and several experimental test procedures for this research. The specific details on response surface methodology (RSM) used in this study were explained clearly in this chapter. According to a previous study, all standards used in experimental procedures and setup were justified clearly.

Chapter 4 presents the results of characterisations of both oxidisers ammonium perchlorate (AP) and potassium permanganate (KMnO_4) and dual oxidisers in terms of morphological, physical, and thermal properties. Furthermore, the effect of dual oxidiser (AP/ KMnO_4) on the production of hydrochloric acid gas (HCl) as a combustion product was discussed. The mechanical properties of CSP with AP/ KMnO_4 as oxidiser were also analysed. As the final objective, the burn rate behaviour of conventional AP-based CSP

and AP/KMnO₄-based CSP were determined and compared. Finally, Chapter 5 summarises the overall findings obtained from the current study and recommendations for future research studies.

done.

1.6 Significant of The Study

Investigating the effects of metal additives in HCl reduction in solid propellants is a significant study with several implications and potential benefits in rocket propellant development and applications. Some of the impacts of this research study are:

- I. **Emission Reduction:** Understanding how KMnO₄/AP affect HCl reduction is crucial for developing propellants with reduced emissions. Besides, this is particularly important for environmental considerations and complying with regulatory standards.
- II. **Performance Optimization:** The study can lead to the identification of promising materials that reduce HCl emissions and enhance overall propellant performance in rocket propellant technology development.
- III. **Innovation in Propellant Technology:** Discovering new ways to modify and improve propellant formulations contributes to advancements in the field and may lead to developing novel, high-performance propellants.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This chapter revealed the literature reviews related to the rocket propellant class, the nature of composite solid propellant (CSP), environmentally friendly oxidisers, and combustion mechanism properties of CSP, which were carried out in this research. All the previous promising materials used in the current study for this related study were compared according to the problem statements highlighted previously. Besides, a review of the current issue highlighted by other researchers regarding the environmental effect of combustion products and CSP has also been illustrated. The review summary was stated clearly at the end of this chapter.

2.2 Rocket Propellant and The Classifications

Chinese people used gunpowder made from sulphur, saltpetre, and other materials in bamboo tubes that they threw into the fire for fireworks during religious and other festivals in the first century A.D (Heister et al., 2019). The original creator of rockets is credited to the Chinese Feng Jishen (970 A.D.) (Liu et al., 2020). At the Battle of Kai-Keng in 1232, the Chinese used a flurry of flying fire arrows, which resembled a basic version of a solid-propellant rocket, to drive back the Mongol invaders. During the 1200s, the Tatars and Moors utilised rockets to invade Europe. Polish artillery specialist Kazimierz Siemienowicz released a set of sketches for a staged rocket in 1650. Through his three principles of motion, Sir Isaac Newton created the groundwork for

contemporary rocketry. The rocket equation was created by Russian mathematician Konstantin Tsiolkovsky (1857–1935), who also wrote on space travel, artificial satellites, and multistage rockets. Over 800 years ago, the Chinese invented and employed solid propellant in rocket missiles, and military bombardment rockets were widely used in the eighteenth and nineteenth centuries (Taylor et al., 2017). However, essential advances in rocket propulsion occurred throughout the twentieth century. Among the early pioneers was the Russian Konstantin E. Ziolkowsky, who was recognised for formulating the essential rocket flight equation and suggesting rocket vehicles in 1903. German physicist Hermann Oberth developed a refined mathematical theory and advocated for multistage spacecraft with fuel-cooled thrust chambers (Oztan et al., 2021). In 1926, the American Robert H. Goddard achieved the first flight with a liquid propellant rocket engine (Jiang et al., 2019). Eugen Sanger, a Viennese engineer, wrote an early treatise on the subject. Solid-propellant rockets are comparatively simple to build since they lack feed systems and valves in liquid and hybrid versions (Ross et al., 2018). Thus, the earliest rockets were solid-fuel rockets powered by gunpowder; they were used in warfare by the Chinese, Indians, Mongols, and Arabs as early as the thirteenth century. Rocket engines, which are non-air-breathing engines, have the following advantages over air-breathing engines (Emrich et al., 2023):

- I. Thrust is fundamentally unaffected by altitude and velocity.

- II. The thrust-to-frontal area ratio is the highest among all known propulsion systems, whilst the supercharged reciprocating engine has the lowest ratio.
- III. The thrust-to-weight ratio of the engine is the highest among all known propulsion systems.
- IV. No altitude limit ceiling or depth restriction.

Rocket propellant is a compound substance or mixture of materials utilised to generate thrust in a rocket engine. The combination of fuel and oxidiser undergoes combustion, generating high-speed exhaust gases that drive the rocket in the opposite direction, in accordance with Newton's third law of motion (Lin et al., 2018). Chemical and non-chemical rockets are the two types of rocket propulsion systems. Rocket propulsion systems are classified based on their energy source (chemical, nuclear, or solar), basic function (booster stage, sustainer, attitude control, orbit station keeping, and so forth), vehicle type (aircraft, missile, assisted take-off, space vehicle, among others), dimensions, propellant type, construction type, or number of rocket propulsion units employed in each vehicle (Gnanaprakash et al., 2018). Another technique is to categorise based on the mechanism of providing thrust. The bulk of viable rocket propulsion designs rely on the thermodynamic expansion of a gas. Fundamentally, the internal energy of the gas is transformed into the kinetic energy of the exhaust flow, and the thrust is created by the gas pressure on the surfaces exposed to the gas (Mao et al., 2019). Some aerospace propulsion systems, such as jet propulsion, rocket propulsion, nuclear propulsion, laser propulsion, solar-thermal propulsion, and other electrical propulsion, all employ the same thermodynamic theory and general

equipment, specifically nozzle. Alternative forms of electric propulsion employ distinct methods of creating thrust, such as using a pendulum in a gravity gradient (Kimura et al., 2016). These electrical systems employ magnetic and/or electric fields to accelerate electrically charged molecules or atoms at very low densities. A rocket engine, known as a rocket motor, is the most essential part of a rocket propulsion system because it is where the propellant's combustion process to generate thrust occurs (Mazzetti et al., 2016). Furthermore, a rocket motor consists of various components, including a motor casing, a combustion chamber (commonly referred to as the propulsion chamber), an exhaust nozzle, a propellant grain, and an igniter (Pérez-Roca et al., 2019). Additionally, they may include control system equipment, especially for the modern rocket propulsion system where thrust vector modelling nozzles are implemented. Figure 2.1 shows the essential parts of the rocket propulsion system.

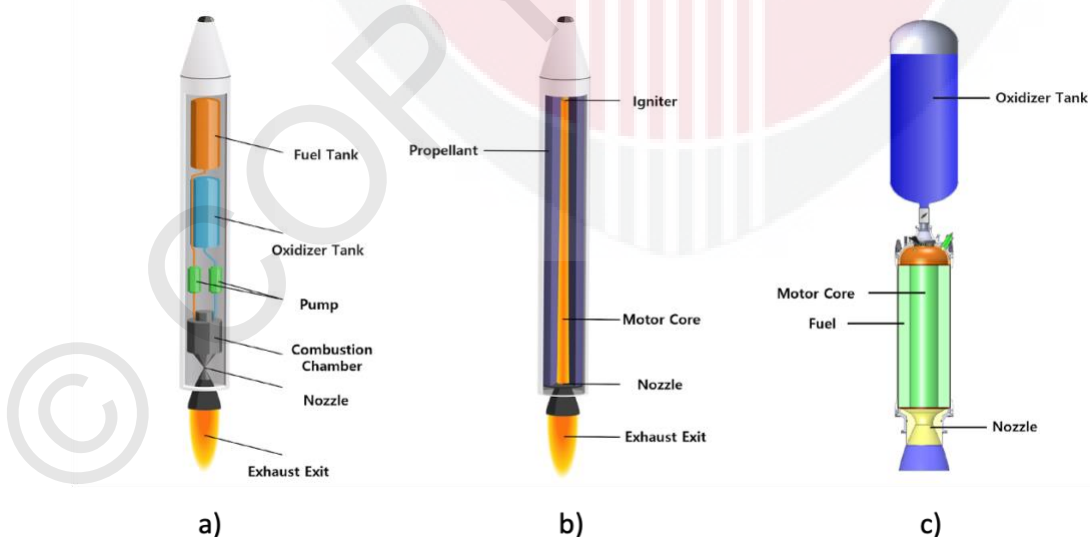


Figure 2.1: Rocket propulsion systems (a) liquid-propellant rocket engine, (b) Solid-propellant rocket motor, and (c) Hybrid-propellant rocket motor

(Source: Cha et al., 2023)

The energy generated by a high-pressure combustion reaction of propellant chemicals, often a fuel and an oxidiser, allows the reaction product gases to reach exceedingly high temperatures (2500°C to 4100°C or 4500°F to 7400°F) (Roy et al., 2016). These gases are further expanded in a nozzle and propelled to high velocities (1800-4300 m/s or 5900-14,100 ft/s) (Simontacchi et al., 2019). Given that these gas temperatures approximate twice the melting point of steel, any surfaces exposed to the hot gases must be either cooled or insulated. Regardless of physical entity, all chemical propellants have the desired qualities for high-level performance. Each propellant must possess superior energetic properties that enable a faster heat release rate alongside elevated combustion temperature, characteristic velocity, and specific impulse (Roy et al., 2016; Schmierer et al., 2019). Aside from that, the propellant must have good ballistic characteristics, including low density, higher ignitability, reproducibility, and low combustion instability (Hargus et al., 2018). The utilisation of low-density propellants necessitates bigger storage tanks, hence augmenting the mass of the launch vehicle. Other desirable attributes of propellants include storage stability, less prone to explosion hazards, smokeless exhaust, low cost, and ease of manufacturing. According to Bennewitz et al. (2018), the following are some of the most prevalent desirable qualities of chemical propellants:

- I. The propellant must exhibit a fast rate of chemical energy release to achieve a higher combustion temperature, resulting in a high characteristic velocity (C^*).

- II. A low molecular weight combustion product results in a high exhaust velocity (V_e) and, as a result, a high specific impulse (I_{sp}).
- III. It can possess a high energy density so that a significant quantity of chemical energy can be stored in the shortest container possible, allowing for a compact design.
- IV. Easy to ignite, even at low pressure.
- V. Consistently stable both physically and chemically throughout time.
- VI. Nature is smoke-free and harmless.
- VII. Cost-effective and straightforward to manufacture and operate.
- VIII. It is readily available.
- IX. Is less likely to cause an explosion.
- X. Low levels of emission.

Chemical propellants are classed based on their physical states, which are liquid, solid, or hybrid, as shown in Figure 2.1. Solid propellants store and combine fuel and oxidiser in a solid state. It should be noted that a solid propellant requires a low ignition temperature for ignition to occur (Frolov et al., 2018). The propellant charge is known as the "grain" because it comprises all the chemical elements required for complete combustion. Once ignited, the charge typically burns smoothly and at a roughly consistent pace on the exposed surface. Based on the distribution of fuel and oxidiser in the propellant, solid propellants can be generically classified as homogeneous or heterogeneous. Fuel and oxidiser are included in the same propellant molecule in the case of homogeneous propellants (Tizón et al., 2017). Solid fuel and oxidiser retain their physical identities in the case of heterogeneous

propellants. Based on Heeg et al. (2020), homogeneous propellants are divided into two types: (1) single base and (2) double base. A single-base propellant, in general, is a single compound that comprises both fuel and oxidiser. In a liquid system, the fuel and oxidiser are kept apart and sprayed into the combustion chamber at high pressures (1900–5500 kPa), resulting in the production of high-temperature (about 4000 K) gases during burning (Schulze et al., 2017). Combustion products go into the nozzle at high speeds, producing a very high thrust. Liquid propellants offer various advantages over solid propellants, and they are commonly utilised when a higher specific impulse is required. Liquid propellants are categorised into two types based on their manner of ignition: hypergolic and non-hypergolic. Liquid fuel and oxidiser react spontaneously in hypergolic propellants without external ignition energy. For example, hydrazine can be called a hypergolic propellant since it conducts exothermic reactions and spontaneously decomposes into water and oxygen when in contact with an appropriate catalyst, even at room temperature (Farooq et al., 2021). However, in the case of non-hypergolic propellants, sufficient ignition energy is delivered to ignite the liquid fuel and oxidiser and allow combustion to occur. A hybrid propellant is a mixture of solid and liquid recently employed in ram rocket engines. Besides, hybrid rocket propulsion is a type of rocket propulsion system that combines elements of both liquid and solid rocket systems. In a hybrid rocket, one of the propellants is in a liquid state, while the other is in a solid state. Solid-propellant rockets are comparatively simple to build since they lack feed systems and valves seen in liquid versions (Urbano et al., 2016). Moreover, in the application of missiles, tactical rocket systems, and low earth orbit rocket vehicles, solid

propellant rockets are the most propellant type used as they are more feasible and practical for processing, costing, and safety. The details of each propellant system will be discussed further in the following sub-chapter.

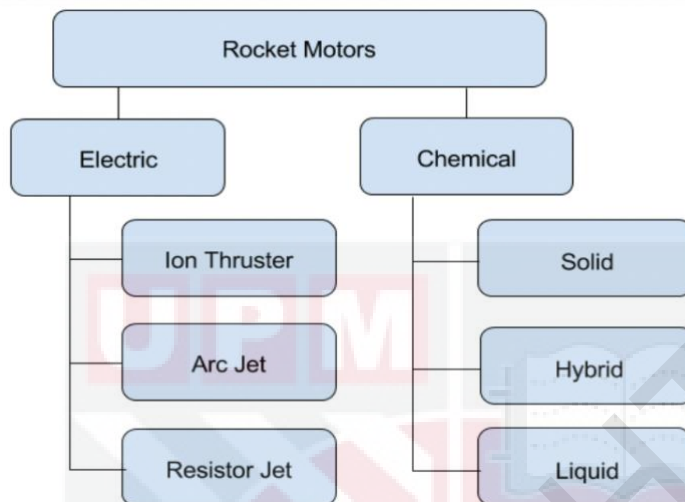


Figure 2.2: Rocket propellant motors classification
(Source: Westerlund et al., 2015)

2.2.1 Liquid Rocket Propellant

Liquid rocket propellants are propellants in a liquid condition. It is also employed as rocket fuel based on Newton's equations of motion. This propellant, referred to as cryogenic propellant, was utilised in the Centaur and Saturn space missions during the late 1950s and early 1960s. Liquid hydrogen is among the most environmentally benign propellants, as it reacts with oxygen as an oxidiser to produce water and traces of ozone and hydrogen peroxide (Altman et al., 2015). However, the process is not so straightforward within the combustion chamber. Steam catalytically interacts with nickel at temperatures between 700-800 °C to produce hydrogen and carbon monoxide. As a result, its production costs are considerably high. The propellant has a density of

0.071 g/ml, resulting in a low molecular weight for exhaust and hence boosts the impulse (Popov et al., 2015). However, space agencies attempt to refrain from utilising this propellant until absolutely necessary. When utilised in a rocket, this propellant requires turbo pumps running at 40,000 rpm, followed by complex ground support systems, including propellant storage and filling systems (Ide et al., 2015). They necessitate individual boosters for a high fuel flow rate into the combustion chamber and regulators to control the flow and thrust, respectively. It possesses a specific impulse of 351s at sea level. It is frequently utilised in rockets such as the DELTA IV, GSLV (Geosynchronous Satellite Launch Vehicle), Centaur, and others. Liquid oxygen and gasoline are the first fuels in liquid propellants. The gasoline utilised is RP-1, characterised by the chemical formula $C_nH_{1.953n}$ with a boiling point range of 177-274 °C (Pylypenko et al., 2020). Table 2.1 shows the standard materials and chemicals used in liquid propellants.

Table 2.1: Liquid propellant standard composition and their properties

Fuel (Formula)	Ammonia (NH ₃)	Aniline (C ₆ H ₅ NH ₂)	Ethyl- Alcohol (C ₂ H ₅ OH)	Furfuryl- Alcohol (C ₅ H ₆ O ₂)	Hydrazine (N ₂ H ₄)	Dimethyl Hydrazine ((CH ₃) ₂ N ₂ H ₂)	Triethylamine ((C ₂ H ₅) ₃ N)	Kerosene (C ₁₀ H ₂₀)	Hydrogen (H)
Molecular weight (kg/kmol)	17.032	93.12	46.06	98.1	32.05	60.1	101.19	140	2.016
Density (kg/m³)	680 (At 239 K)	1012 (At 298 K)	785 (At 298 K)	1129 (At 298 K)	1011 (At 288 K)	808 (At 288 K)	723 (At 288 K)	800 (At 298 K)	70.21 (At 20.5 K)
Melting point (K)	195.42	279.6	158.6	241.2	274.7	215	158.2	230	13.96
Specific heat	4.4	2.01	2.59	2.43	3.14	2.69	1.89	2.0934	7.327
Heat of formation (kJ/mol) (at 298 K)	-46.2	34.3	-278	-142.35	50.45	47.31	-154.912	-247.021	N/A
Thermal conductivity (kJ/ms•K) x 10⁵	5	17.7	16.7	N/A	20.9	20.76	12.09	0.0001	0.0000662

N/A: Not applicable
(Source: Pérez-Roca et al., 2019)

2.2.2 Solid Rocket Propellant

Solid rocket propellants are inherently solid substances used for propulsion. It serves as an energetic particle in numerous applications, including space shuttles and military munitions. This propellant offers various intriguing properties, such as simplicity, dependability, storage capability, high thrust, mass flow during launching, and so on (Mason et al., 2019). The two essential ingredients necessary to classify it as a solid propellant are fuel and oxidiser. Several additions, such as nanoparticles (graphene, carbon nanotubes), are required to improve the propellant's characteristics. The basic mechanics of a solid propellant involves positioning a cast solid propellant inside a combustion chamber and igniting it. The combustion initiates as the propellant ignites, releasing gases from the nozzle on the lower side, generating a force on the surface. Consequently, in accordance with Newton's third law of motion, this results in an opposing force that propels the rocket into the atmosphere (Lysien et al., 2021). The fuel-oxidiser mixture is ignited by a spark at the throat area, resulting in combustion within the combustion chamber.

Parameters are the fundamental metrics on which solid propellant is evaluated for its functionality. However, the rocket's design significantly influences the application of the solid propellant, including casing design based on combustion chamber pressure, nozzle design based on burn rate, and the surface area required by the fuel oxidiser chamber to hold the solid propellant until propulsion occurs (Arkhipov et al., 2016). Several factors influence this fuel's ability to be employed as a propellant. The temperature of the rocket motor chamber is among the most critical factors, followed by unconditional

propellant grain burning (Huggett et al., 2015). Due to these significant factors, rocket propulsion has become exceedingly challenging and costly, necessitating the exploration of alternative fuel sources. In addition, a solid propellant's molecular organisation and grain size are critical factors in its evaluation as a propellant. This is because the grains must be distributed evenly during combustion to ensure that the force created is directed appropriately.

Black powder, also known as gunpowder, was the earliest form of solid propellant used, according to (Wibowo et al. (2018). This propellant utilised sulphur as fuel and potassium nitrate as an oxidiser, with charcoal also included in the mixture. Sulphur served an additional role as a catalyst, as noted by Vo et al. (2018). However, its use was often linked to catastrophic failures due to its low impulse and thrust levels.

For zinc sulphur propellant, the fuel is zinc metal, while the oxidiser is sulphur. The zinc sulphur propellant is known for its performance and rapid linear burn rate (Emelyanov et al., 2020). Besides that, candy propellant, which used dextrose, sucrose, and sorbitol as sugar fuels and potassium nitrate as the oxidiser, exhibited a low specific impulse (Varghese et al., 2017). The composite propellant, comprising a mixture of oxidiser, metal, and powder-form binder fuel, represents a more advanced stage in solid propellant development. Solid propellant is categorised into two types: heterogeneous and homogeneous solid propellant. Homogeneous propellant contains the oxidiser and fuel mixed together on a molecular level. In contrast,

heterogeneous or composite propellants contain solid composite fuel particles and solid oxidiser particles, which are not intimately intermixed on the molecular level. Figure 2.3 shows the classification of solid rocket propellant.

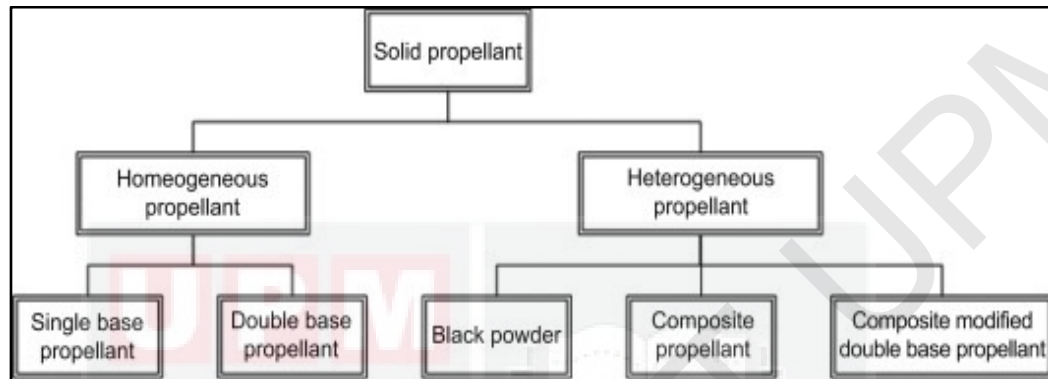


Figure 2.3: Solid rocket propellant classification
(Source: Micci et al., 2000)

Compared to AN-based composite on aluminium as fuel, AP-based composite propellants with magnesium/aluminium base fuel perform better (Cui et al., 2020). Aluminium powder impacted combustion efficiency, burning rates, combustion efficiency, and two-phase flow losses. The main disadvantage of aluminium is the buildup of all aluminium oxide slag near the rarier chamber region close to the nozzle (Genevieve et al., 2017). It impacts critical rocket propellant parameters, including thrust thermal insulator and specific impulse. Reducing the size of aluminium powder can significantly influence the propellant's characteristics. By conducting a structural analysis of this solid propellant, considering variations in particle size, its performance could be enhanced. The composition of AP-based composite propellant comprises 69-70% AP as oxidiser and 16-20% fine aluminium powder as the metal fuel. One of the greatest and finest discoveries in the field of solid propellant is the

incorporation of 11-14% PBAN/HTPB as a binding agent, achieving a specific impulse of 277 s (Kim et al., 2018). Solid propellants are also categorised as:

- I. Composites comprise a mixture of solid oxidiser granules (e.g., ammonium nitrate, ammonium dinitramide), ammonium polyoxometalate and potassium nitrate (KNO_3) together with polymer binding agents and particles or powder of energetic fuel compounds.
- II. A homogeneous mixture of mono, bi, and tri bases containing one to three primary constituents. Specific substances possess dual or multipurpose characteristics. For instance, nitrocellulose serves as both a fuel and an oxidiser, while RDX (Research Development Explosives) functions as both a fuel and an oxidiser (Pérez-Roca et al., 2019).

Compared to liquid propellant, solid propellant is the most practical for use in military tactical rockets, interceptor missiles, and sounding rockets for low earth orbit missions. This is because solid propellant has several tremendous properties compared to liquid propellants, as revealed in Table 2.2.

Table 2.2: Solid and liquid propellant comparison

No.	Solid Propellants	Liquid Propellants
1.	Low specific impulse	High specific impulse
2.	Easy to store, handle, and transport	Difficult to store, handle, and transport
3.	Simple to design and develop solid-propellant rocket engine	Complex to design and develop a liquid-propellant rocket engine
4.	More economical	Less economical

(Source: de Iaco Veris et al., 2021)

2.2.3 Hybrid Rocket Propellant

Hybrid rocket propellant, a novel development in propulsion technology, leverages solid fuel and liquid oxidiser to enable combustion (Betelin et al., 2018). The design incorporates the liquid oxidiser being introduced before the combustion chamber, which holds the solid propellant that has been cast. The oxidiser chamber houses the valve, allowing the liquid to follow for ignition. Hence, this valve aids in thrust regulation (Gieras et al., 2021). Subsequent to this valve, an injector atomises the liquid oxidiser in the combustion chamber to ensure homogeneous solid propellant burning. The nozzle beneath the combustion chamber aids in increasing the velocity of the gases produced. A turbo pump or a gas chamber is utilised to inject the liquid propellant to oxidise the solid fuel for combustion. This hybrid approach offers several benefits over conventional solid and liquid propellants, marking a significant milestone in propellant research (Lee et al., 2017). Commonly utilised oxidisers include N_2O_4 (dinitrogen tetroxide), RP-1 (rocket propellant), CH_4 , LH_2 (liquid hydrogen), and LOX (liquid oxygen) (Gallo et al., 2021). The most frequent fuels are (i) Hydroxyl-terminated polybutadiene (HTPB), (ii) Acrylonitrile butadiene styrene (ABS), (iii) gunpowder, (iv) polyethylene, and (iv) several additional substances under an investigation like paraffin wax with additions such as aluminium, carbon nanotubes, graphene (Buturache et al., 2018). Compared to its counterparts, this hybrid propellant stands out due to its lower density, reduced storage requirements, higher thrust, and cost-effectiveness (Chen et al., 2018). However, challenges exist, such as an unconventional oxidiser-to-fuel ratio. After complete combustion, the solid propellant left some particles in the chambers at the end, reducing acceleration or thrust to a small

amount and diminishing propulsion efficiency. The amount of solid propellant utilised is a 2-dimensional matrix and grain size, resulting in a low regression rate. Moreover, issues such as poor burning rates, toxicity, and the hazardous nature of the by-products pose significant drawbacks (Casalino et al., 2018). In addition to its combustion products, the hybrid rocket's propellant faces challenges that will lead to non-practical rocket propellants for some applications. Some drawbacks of hybrid rocket propellants are complex design, limited fuel options, and uneven combustion performance. Table 2.3 illustrates some differences between hybrid and solid rocket propellants, as Akhter et al. (2020) explained.

Table 2.3: Comparison between solid and hybrid rocket propellant

Parameter	Solid Propellants	Hybrid Propellants
Dominating combustion mechanism.	Chemical kinetics.	Heat transfer.
Main parameter governing regression.	Combustion chamber pressure.	Oxidiser mass flux.
Main parameters governing operating point.	Combustion chamber pressure. Clamping (ratio of burning area to port area).	Oxidiser mass flow rate. Geometry of solid fuel grain.
Other parameters influence the regression rate.	Combustion temperature. Particle size of oxidiser. Propellant composition. Initial grain temperature. Gas velocity. Propellant configuration	Composition of solid fuel grain. Melting point. Flame temperature. Combustion chamber pressure.

(Source: Akhter et al., 2020)

2.3 Solid Propellant Rockets (SPRs) Motor

Solid propellant rockets (SPRs) have been used for various purposes and are said to have been invented by the Chinese and Indians following the discovery of black powder. SPRs have seen significant advancements in recent years. As a result, they now have a wide variety of applications in the form of different propulsive devices, such as spacecraft, missiles, airplanes, retro rockets, and gas-generating systems. It has been utilised in anti-tank and anti-aircraft missiles because of its great dependability, even exceeding 99%, and lightweight (Mishra et al., 2017). The pressure in an SPR combustion chamber is often substantially higher than in a liquid propellant rocket, resulting in a more significant thrust coefficient (Pradhan et al., 2020). They can produce thrust ranging from a few milli-Newtons to meganewtons. As mentioned in the previous chapter, SPRs are chosen over conventional chemical rocket engines in situations requiring great dependability, fast operating readiness, and easy storage. Unlike the liquid propellant rocket, the SPRs have no moving components unless a thrust vector control system is installed (Huggett et al., 2015). It is also referred to as a solid propellant rocket motor on various occasions. It comprises a propellant grain, an igniter, a motor casing, a thermal insulator, a nozzle, and a thrust terminator, as illustrated in Figure 2.4. The motor casing that holds the propellant grain is typically composed of high-strength, temperature-resistant materials that are covered with organic compounds that not only function as a thermal insulator but also provide light bonding between the propellant grain and the chamber wall (Shukla et al., 2017). The rocket engine casing is often made of steel, titanium, and aluminium alloys, which can sustain high stress levels, particularly at high

pressure and temperature. Designers have recently begun to use fibre-reinforced composite materials, which are substantially lighter than metal casing. A particular shape of propellant grain is employed to provide a specific sort of thrust and time profile. The propellant grain in a typical solid rocket engine accounts for around 85% of the overall mass of the rocket engine (de Iaco Veris et al., 2021). A wall, retainer push (thermal insulators), or customised grids or traps often support the propellant grain. The insulated nozzle and the igniter are the other important motor components.

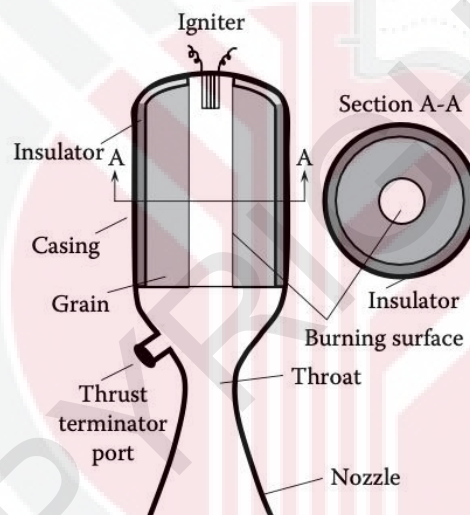


Figure 2.4: Typical solid propellant rocket motor design

(Source: Sreejith et al., 2021)

The ingredients are chemically linked in inhomogeneous propellants, creating a uniform structure. Examples of homogeneous propellants include single-base nitrocellulose (NC) and additive, double-base NC, nitro-glycerine (NG), and additives, and triple-base NC, NG, nitroguanidine (NQ), and additives propellants (Davenas et al., 2012). On the other hand, heterogeneous or composite propellants are formed through the physical mixing of components,

leading to a structurally diverse material. Crystalline particles function as the oxidiser, while organic plastic fuels serve as the binder to affix the oxidiser particles (Beckstead et al., 1993). Common oxidising agents include Octogen (HMX), ammonium perchlorate (AP), ammonium nitrate (AN), ammonium dinitramide (ADN), and hexogen (RDX).

2.4 Composite Solid Propellant (CSP) in Solid Propellant Rocket Motor Applications

Composite solid propellant (CSP) comprise crystalline oxidiser particles bonded to a polymeric fuel matrix. Ammonium perchlorate (AP) and ammonium nitrate (AN), extensively used oxidisers, yield substantial oxygen concentrations after thermal decomposition. The fuel utilised is hydrocarbon-based polymers such hydroxyl-terminated polybutadiene (HTPB), N-(4-chloro-3-trifluoromethyl-phenyl)-2-methoxy-6-pentadecyl-benzamide (CTPB), and polybutadiene acrylonitrile (PBAN). Typically, high oxidiser concentrations provide a strong specific impulse (Garino et al., 2021). Aluminium particles are often added to boost impulse as metal fuel. Upon combustion, AP-based composite propellants typically emit white vapour. This is because hydrochloric acid gases (HCl), one of the by-products of combustion, initiate the condensation of atmospheric moisture, producing fog or mist (Vijay et al., 2019). Although the use of AN prevents the production of such fumes, it diminishes efficacy due to the decreased specific impulse. The AP/HTPB combination is extensively utilised because HTPB's exceptional binding qualities enhance combustion performance and impart desirable physical and mechanical properties to the propellant. In conjunction with AP or AN, azide

polymers like glycidyl azide polymer (GAP) and 3,3-Bis(azidomethyl)oxetane (BAMO) are utilised to create composite propellants (McClain et al., 2021). The introduction of metallic fuel, such as aluminium, into composite propellants results in a substantial elevation of the adiabatic combustion temperatures. When aluminium is utilised, a significant quantity of aluminium oxide (Al_2O_3) is predominantly found in the liquid phase within the combustion products of the chamber (Naseem et al., 2021). Thus, composite-based propellant is the most common type of solid propellant used in a wide area of propellant field, especially in missiles.

2.4.1 Composite Solid Propellant (CSP) Composition and Formulations

For over 50 years, composite propellants based on ammonium perchlorate (AP) have been a mainstay in solid rocket propulsion. AP (NH_4ClO_4) granules, which range in size from 20 to 200 μm , are usually distributed in a multimodal manner inside the hydroxyl-terminated polybutadiene (HTPB) polymer matrix of this kind of propellant (Kebritchi et al., 2018). Gas-phase reactions, melting and surface pyrolysis, AP and HTPB degradation, condensed-phase heating, and other physicochemical processes take place during the combustion of AP/HTPB propellant. Several variables, including propellant composition and formulation, AP grain size, initial and ambient conditions, and propellant morphological configuration, affect the propellant grain's flame structures and burning behaviour (Lin et al., 2018). Besides, the formulation of the propellant composition is very crucial as the choice of this will vary the performance of the propellant grain as different formulations will result in different

characteristics of the propellant slurry, the mechanical properties, and thermal behaviour (Hu et al., 2019).

High specific impulse, predictable and reproducible burning rate and ignition properties, high density, ease of production, cheap cost, and acceptable ageing characteristics are desirable for a solid propellant (Zeng et al., 2019). Propellant grain should emit low-smoke exhaust and be resistant to combustion instability from a safety standpoint (Dallas et al., 2020). Furthermore, they must have appropriate thermophysical and mechanical qualities across the desired working and storage conditions. Solid propellants are often classed as homogeneous or heterogeneous due to their chemical composition and physical structure. Fuels and oxidisers are chemically connected at the molecular level in the former. Fuel and oxidisers are physically combined in the latter. The components of homogeneous propellants come from a variety of chemical families, predominantly classified into four categories: nitramines (RDX, HMX, HNIW, also known as CL-20, HNF), azides (GAP, BAMO, AMMO), nitrate esters (NG, NC, BTTN, TMETN, DEGDN), or nitrates (ADN, AN) (Biliaiev et al., 2019). Oxidisers, including AP, AN, and KN, and fuels such as HTPB, HTPE, and CTPB, are frequently used in composite propellants (Rettinger et al., 2019). The general regions of specific impulse, combustion rate, and density for the more prevalent categories of propellants are illustrated in Table 2.4.

Table 2.4: Solid propellant formulation characteristics

Propellant Type	Specific Impulse, I_{sp} Range (s)	Density (lb/in ³)	Metal Content (wt. %)	Burning Rate (mm/s)	Hazard classification	Stress (psi)/Strain (%)	
						-600F	+1500F
DB	220-230	0.058	0	0.05-1.2	1.1	4600/2	490/60
DB/AP/Al	260-265	0.065	20-21	0.2-1.0	1.3	2750/5	120/50
DB/AP-HMX/Al	265-270	0.065	20	0.2-1.2	1.1	2375/3	50/33
PVC/AP/Al	260-265	0.064	21	0.3-0.9	1.3	369/150	38/220
PU/AP/Al	260-265	0.064	16-20	0.2-0.9	1.3	29 1/3	75/33
PBAN/AP/Al	260-263	64	16	0.25-1.0	1.3	520/16	71/28
CTPB/AP/Al	260-265	0.064	15-17	0.25-2.0	1.3	325/26	88/75
HTPB/AP/Al	260-265	0.067	4-17	0.25-3.0	1.3	910/50	90/33
PBAA/AP/Al	260-265	0.064	14	0.25-1.3	1.3	500/13	41/31
AN/Polymer	180-190	0.053	0	0.06-0.5	1.3	200/5	NA

(Source: Sutton et al., 2016)

Based on the literature in Table 2.4, HTPB/AP/Al composite propellants exhibit an expanded spectrum of burning rates, increased specific impulse, and greater densities compared to others. Conventional composite propellants typically comprise 60 to 72% crystalline oxidiser ammonium perchlorate (AP), up to 22% metal fuel aluminium powder (Al), and 8 to 16% elastomeric binder (organic polymer) plus its plasticiser (Varghese et al., 2017). The choice of propellant is crucial in rocket motor design. The desirable propellant properties are described, and the common materials and chemicals with their weight percentage in AP-based composite solid propellant are illustrated in Table 2.5.

Table 2.5: Common materials and chemicals for composite solid propellant (CSP)

Type	Weight percentage (%) in propellant formulation	Typical Chemicals
Oxidiser (crystalline)	0-70	Ammonium perchlorate (AP), Ammonium nitrate (AN), Potassium perchlorate (KP), Potassium nitrate (KN), Ammonium dinitramide (ADN)
Metal fuel (also acts as a combustion stabiliser)	0-30	Aluminium (Al), Beryllium (Be) (experimental propellant only), Zirconium (Zr) (also acts as burn-rate modifier)
Fuel/Binder, polybutadiene type	5-18	Hydroxyl-terminated polybutadiene (HTPB), Carboxyl-terminated polybutadiene (CTPB), Polybutadiene acrylonitrile acrylic acid (PBAN), Polybutadiene acrylic acid (PBAA)
Fuel/Binder, polyether, and polyester-type	0-15	Polyethylene glycol (PEG), Polycaprolactone polyol (PCP), Polyglycol adipate (PGA), Polypropylene glycol (PPG), Hydroxyl-terminated polyethylene (HTPE), Polyurethane polyester or polyether (PU)
Curing agent or crosslinker, which reacts with polymer	0.2-3.5	Methyl aziridiny phosphine oxide (MAPO), Isophorone diisocyanate (IPDI), Toluene-2,4-diisocyanate (TDI), Hexamethylene diisocyanate (HMDI), Dimethyl diisocyanate (DDI), Trimethylolpropane (TMP), Trimesoyl- 1 (2-ethyl)-aziridine (BITA)
Burn-rate modifier	0.2-3	Ferric oxide (FeO), n-butyl ferrocene (nBF), Oxides of Cu, Pb, Zr, Fe, Alkaline earth carbonates, Alkaline earth sulphates, metallo-organic compounds
Explosive filler (solid)	0-40	Cyclotetramethylenetetranitramine (HMX), Cyclotrimethylenetrinitramine Nitroguanidine (RDX), Nitroguanidine (NQ)
Plasticizer/Pot life control (organic liquid)	0-7	Diethyl phthalate (DOP), Dioctyl adipate (DOA), Dioctyl sebacate (DOS) Dimethyl phthalate (DMP), isodecyl pelargonate (IDP)

Table 2.5: (continued)

Type	Weight percentage (%) in propellant formulation	Typical Chemicals
Energetic plasticizer (liquid)	0-14	Glycidyl azide polymer (GAP), Nitroglycerine (NG), Diethylene glycol dinitrate (DEGDN), Butanetriol trinitrate (BTTN), Triethylene glycol dinitrate (TEGDN), Trimethylolethane trinitrate (TMETN), Polycaprolactone polymer (PCP)
Energetic fuel/binder	0-15	Glycidyl azide polymer (GAP), Propylglycidyl nitrate (PGN), Bis-azidomethyl oxetane (BAMO) /Nitro Methyl methyl oxetane copolymer (NMMO)
Bonding agent (improves bond to solid particles)	>0.1	MAPO-tartaric acid-adipic acid condensate (MT-4) Bis-isophthal-methyl-aziridine (HX-752)
Stabilizer (reduces chemical deterioration)	>0.5	Diphenylamine Phenylnaphthylamine (DPA), N-methyl-p-nitroaniline Dinitrodiphenylamine (NMA)
Processing aid	>0.5	Lecithin, Sodium lauryl sulphate

(Source: Feodosiev et al., 2014)

2.4.2 Type of Oxidiser Used in Solid Propellant Rocket Applications

Oxidisers are the primary components responsible for generating high energy during combustion. AP is at the top of the oxidiser list due to its strong performance, availability, and compatibility with other propellant components, among other advantages. There are circumstances in which ammonium nitrate (AN) and potassium nitrate (KN) are also applied. Despite possessing a lower oxidation efficiency than perchlorates, inorganic nitrates continue to be utilised owing to their low cost and odourless, non-toxic emissions (Dalinger et al., 2018). In the 1970s, many oxidiser compounds were studied, but none were produced (Zamostianu et al., 2022). Because perchlorates often have a high oxidising potential, this material is well suited for high specific impulse propellants. Potassium and ammonium perchlorate have low water solubility, which is advantageous for propellant applications. When perchlorate oxidisers react with fuels, they create hydrogen chloride (HCl) and other hazardous and caustic chlorine chemicals (Mason et al., 2019). Rocket firing requires caution, especially for very big rockets, to protect operational staff and nearby towns from exhaust gas clouds. The size and form of the particles influence the propellant burning rate and the manufacturing process. Close monitoring of the crystal sizes and size distribution in a particular batch or amount is therefore necessary. AP crystals mix more easily than jagged, broken crystals because they are rounded, almost ball-shaped. From the manufacturer, they are available in diameters of around 600 μm ($1 \mu\text{m} = 10^{-6} \text{ m}$) to approximately 80 μm . The propellant manufacturer does not ship sizes smaller than 40 μm in diameter because they are deemed dangerous due to their easy ignition and occasional detonation (Wibowo et al., 2018). Instead, the larger crystals

are ground down to only 2 μm at the motor factory before being incorporated into a propellant.

When opposed to perchlorates, inorganic nitrates have somewhat lower oxidation performance. However, because of its extremely low cost and smokeless, mostly harmless exhaust, ammonium nitrate is employed in several applications (Simontacchi et al., 2019). Its main applications are gas generators and rockets with limited performance and low burning rates. At various phase transformation temperatures, ammonium nitrate (AN) changes its crystal structure (Shukla et al., 2017). Slight variations in volume result from these modifications. At 32°C, a single-phase transition results in a volume change of around 3.4%. Frequent cycling of the temperature across this transition point results in the expansion of the grain, the creation of microscopic gaps in the propellant, and a modification of the physical or ballistic characteristics. According to (Chen et al., 2018), it shows that adding a tiny quantity of stabiliser, such as potassium nitrate (KNO_3) or nickel oxide (NiO), appears to shift the transition temperature to over 60°C, a high enough value that typical ambient temperature cycling will no longer produce recrystallisation. Phase-stabilized ammonium nitrate is the term for AN with this addition (PSAN). Because AN is hygroscopic, the propellant produced by AN will deteriorate when moisture absorbs into it (Singh et al., 2019). Table 2.6 shows the conventional oxidiser used in composite solid propellant.

Table 2.6: Common crystalline oxidisers and their properties used in AP-based solid propellant rockets

Oxidiser	Chemical Symbol	Molecular Weight	Density (kg/m ³)	Oxygen Balance (%)	Heat of Formation (kJ/mol)	Reference
Ammonium perchlorate (AP)	NH ₄ ClO ₄	117.5	1.95	34	-296	Kumar et al., 2018
Ammonium nitrate (AN)	NH ₄ NO ₃	80	1.72	20	-369	Oluwoye et al., 2020
Hexogen (RDX)	C ₃ H ₆ N ₃ (NO ₂) ₃	222	1.82	-21.6	70	Kalal et al., 2020;
Octogen (HMX)	C ₄ H ₈ N ₈ O ₈	296	1.91	-21.6	84	Nagendra et al., 2023
Ammonium dinitramide (ADN)	C ₄ H ₈ N ₄ (NO ₂) ₄	124	1.81	25.8	-150	Sergienko et al., 2019
Hexanitrohexaazaisowurtzitane (HNIW) (CL-20)	C ₆ H ₆ N ₁₂ O ₁₂	438	2.04	-10.9	372	Imiolek et al., 2019
Hydrazinium nitroformate (HNF)	N ₂ H ₅ C(NO ₂) ₃	183	1.83	13	-72	Mao et al., 2019
						Dîrloman et al., 2024

2.4.3 Aluminium as Metal Fuel in Composite Solid Propellant (CSP)

Spherical aluminium powder is the most often used fuel for composite solid propellants (GÖK et al., 2020). It comprises tiny spherical particles with a diameter of 5 to 60 μm and is utilised in various double-base propellant formulations, both original and modified by composites. Typically, it makes up about 14 to 20% of the propellant's weight (Glotov et al., 2023). Aluminum has a very high energy content per mass and is characterised by high specific energy conversion rates (about 31.0 MJ/kg) compared to other metal fuels. When aluminum combusts in the presence of an enhancer, the reaction produces tremendous amounts of heat energy, which helps achieve high specific impulse (a defining factor of propulsion efficiency (Kanagarajan et al., 2022)).

2.4.4 Hydroxyl-Terminated Polybutadiene (HTPB) Polymer Binder as A Composite Matrix in Composite Solid Propellant (CSP)

The binder serves as the structural glue or matrix via which solid granular elements of a composite propellant are kept together. Liquid pre-polymers or monomers are the raw components (Yogeshkumar et al., 2020). They produce a hard rubber-like substance that comprises the grain after being combined with the solid components, cast, and cured. Polyvinyl Chloride (PVC) and polyurethane (PU) leather were utilised 40 years ago and are still employed in a few motors, mainly of older design (Ma et al., 2020). Binder materials are also solid propellant rocket fuels that are oxidised during the combustion process. The binding ingredient, generally a polymer of some kind, significantly impacts motor dependability, mechanical qualities, propellant

processing complexity, storability, ageing, and prices (Kirby et al., 2023). During propellant curing, certain polymers undergo complicated chemical reactions, crosslinking, and branch chaining. In recent years, hydroxyl-terminated polybutadiene (HTPB) has been the preferred binder due to its greater solid percentage (88 to 90% AP and Al) and reasonably strong physical qualities at temperature limitations (Yuan et al., 2021). The choice of binder affects the mechanical properties, burn rate, and overall performance of the composite propellant.

2.4.5 Additive Materials in Composite Solid Propellant (CSP) Application

A plasticiser is often a low-viscosity liquid organic component that simultaneously serves as fuel. It is added to increase propellant elongation at low temperatures as well as processing features such as decreased viscosity for casting or longer pot life of blended but uncured propellants (Pinalia et al., 2021). According to (Pang et al., 2020), most plasticisers work by lowering polymers' glass transition temperature (T_g), increasing their flexibility, and making them easier to work with. Besides, it is a low-viscosity organic liquid that contributes to thermal energy during oxidation, which will help in the thermal decomposition of composite solid propellant (Bhowmik et al., 2017).

The use of a plasticiser significantly enhances the processing qualities of the propellant. Besides, the plasticiser helps improve the processing characteristics of the propellant, making it easier to handle and shape during manufacturing (Yan et al., 2020). It also contributes to the propellant's ability to withstand mechanical stresses and temperature variations. In AP-based

CSP, the most common types of plasticisers used are Isodecyl pelargonate (IDP), dibutyl sebacate (DBS), and dibutyl adipate (DOA) (Lemos et al., 2018) and IDP and DOA performed the best as the propellant slurry viscosity produced is the lowest compared to others. However, due to the high cost of IDP raw materials, DOA is used in AP-based CSP. Table 2.7 illustrates the basic chemical structure of IDP and DOA.

Table 2.7: Chemical Structure of Isodecyl Pelargonate (IDP) and Dibutyl Adipate (DOA)

Plasticiser name	Chemical structure
Dioctyl Azelate (DOA)	$\begin{array}{c} \text{COO}-\text{C}_8\text{H}_{17} \\ \diagup \\ (\text{CH}_2)_7 \\ \diagdown \\ \text{COO}-\text{C}_8\text{H}_{17} \end{array}$
Isodecyl Pelargonate (IDP)	$\text{CH}_3-(\text{CH}_2)_7-\text{COO}-\text{C}_{10}\text{H}_{21}$

(Source: Khalil et al., 2016)

A curing agent is used to initiate and accelerate the cross-linking or curing reaction of the binder polymer. The curing process transforms the liquid or semi-liquid binder into a solid, elastic matrix that holds the solid particles (oxidisers, fuels, additives) together, forming a cohesive propellant grain (Zumbo et al., 2024). An isocyanate compound is the most common curing agent used in composite solid propellants. One specific isocyanate often used is toluene diisocyanate (TDI). When mixed with the binder (usually hydroxyl-terminated polybutadiene, HTPB, or another polymer), the isocyanate reacts with the hydroxyl (OH) groups in the polymer, leading to the formation of urethane linkages (Da Cunha et al., 2022). The chemical reaction can be represented as follows:



Small amounts of additives are used for a variety of purposes, such as accelerating or lengthening the curing time, improving the rheological properties (easier casting of viscous raw mixed propellant), improving the physical properties, adding opaqueness to a transparent propellant to prevent radiation heating at locations other than the burning surface, limiting migration of chemical species from the propellant to the binder or vice versa, minimising slow oxidation or chemisorption, and minimising slow oxidation (Kline et al., 2019). Bonding agents are additions that improve the adhesion of the solid materials to the binder. Stabilisers are designed to slow down the chemical and physical processes that can occur in propellants (Collard et al., 2019). Some of the commonly used additives are listed in Figure 2.5.



Figure 2.5: Common types of additives used in composite solid propellant rockets

A propellant burning-rate catalyst aids in increasing or decreasing the propellant burning rate. It is also known as the burning rate modifier at times.

It may be used to set a desired burning rate for a given grain design. A good solid propellant should have a consistent burning rate and a low-pressure exponent, and one of the best methods to achieve this is to incorporate a burning rate catalyst into the propellant (Jain et al., 2019). Nowadays, the most common burning rate catalysts are transition metal oxides, nano-metal particles, metal chelates, and ferrocene and its derivatives (Xiao et al., 2020).

Transition metal oxide burning rate catalysts are simple to make and

inexpensive, yet they do not significantly boost the burning rate. Nano-metal particles have a greater specific surface area and a higher surface energy (Song et al., 2018) and can increase the combustion rate. According to Dirloman et al. (2024), burning rate catalysts are not only a ballistic nature regulator in the solid propellant, but they are also an essential element due to their capacity to improve the burning character and eliminate the propellant's principal smoke. As a result, burning rate catalysts have received much interest. However, finding the perfect materials for burn rate enhancement in AP-based composite propellant is still in progress. This is because the materials for improving the burn rate must be concurrent with the economic issue, method of fabrication, combustion product, and raw materials availability (Kalal et al., 2020).

2.5 Ammonium Perchlorate (AP) as a Primary Oxidiser in Solid Propellant Rocket Applications

Ammonium perchlorate (AP) is the most common energetic material, serving as a crucial oxidiser in solid rocket propellants, including ammonium perchlorate composite propellants (APCP) and the Space Shuttle Solid Rocket Boosters, produced by Alliant Techsystems (ATK). Its application extends to a wide range of solid rockets, such as fireworks and amateur high-powered rockets, as well as space launches and military rockets (Ashish et al., 2019).

Despite its widespread use, AP remains among the lesser-known energetic materials. Numerous publications have been written about AP's decomposition process and structural properties. The decomposition of AP presents a challenge, as this simple molecule is made up of four separate

elements: Nitrogen (N), hydrogen (H), chlorine (Cl), and oxygen (O) (Petersen et al., 2019). Considering these elements' potential oxidation states, AP's disintegration can involve 1000 chemical reactions. Furthermore, the presence of Cl distinguishes AP from other propellant and explosive constituents. Other energetic materials are mostly if not entirely, made up of carbon, hydrogen, nitrogen, and oxygen (Kopacz et al., 2022). Additionally, contaminants can influence AP materials' decomposition, combustion, and burn rate, posing significant challenges. As a result, the reaction chemistry of AP is still mainly in the research stage (McClain et al., 2021). The thermal decomposition properties of AP are critical for the combustion of propellants. AP-based composite solid propellant (CSP) formulations often include combustion modifiers to propellant decomposition to attain greater burning rates.

2.5.1 Physical and Chemical Properties of Ammonium Perchlorate

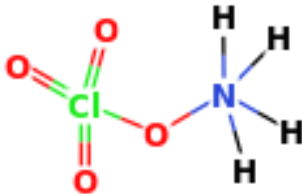
Ammonium perchlorate (AP), a white crystalline solid material with the chemical formula NH_4ClO_4 , is the most commonly used oxidiser in composite solid propellant (CSP). It is odourless, appears as granules, and has a density of approximately 1.95 g/cm^3 in its crystalline form, as in Figure 2.6. AP features a relatively high melting point of about 842°F and decomposes before reaching its boiling point.



Figure 2.6: Ammonium perchlorate (AP) as a white, odourless crystal
(Source: Yeh et al., 2021)

Although sparingly soluble in water, its solubility slightly increases with temperature, yet it remains relatively insoluble. AP has a tetragonal crystal structure and is not highly hygroscopic, meaning it does not readily absorb moisture from the air. However, it can absorb some water under certain conditions, necessitating storage in vacuum conditions or within a propellant desiccator to maintain stability (Tolmachoff et al., 2022). AP is generally stable under normal storage conditions. However, it can decompose exothermically at high temperatures, releasing oxygen and forming ammonium chloride (NH_4Cl) (Manash et al., 2019). AP is a powerful oxidiser; when combined with fuels, it forms a potent propellant. Due to its use in rocketry and pyrotechnics, safety precautions should be taken during handling and storage (Essel et al., 2020). Additionally, the use of AP in specific applications has raised environmental concerns, and its use is subject to regulations in various jurisdictions (Khan et al., 2019). The chemical properties of AP are listed in Table 2.8.

Table 2.8: Chemical properties of ammonium perchlorate (AP)

Parameter	Value
Chemical formula	NH_4ClO_4
Chemical structure	
Molecular weight	117.49 g/mol
Density	1.95 g/cm ³ (at 20°C)
Compatibility	Ammonium perchlorate is often combined with powdered metals (such as powdered aluminium) as a fuel to enhance its performance in rocket propellants.

(Source: Ashish et al., 2019)

2.5.2 Thermal Decomposition Properties of Ammonium Perchlorate as An Oxidiser in Composite Solid Propellant (CSP)

Several scholars have researched and evaluated the gradual disintegration of AP throughout the years. The most recent report by Hu et al. (2019) summarised the research on the slow thermal decomposition of AP. The authors concluded that, despite advances in diagnostic techniques, the complete array of physio-chemical processes occurring on the microstructures formed over and inside the crystals of AP is still beyond the reach of researchers. According to Yan et al. (2018), the catalyst in enhancing AP thermal decomposition can reduce low-temperature decomposition (LTD) and high-temperature decompositions (HTD) and will influence heat release. The decomposition of AP is known to occur in two temperature-dependent phases, the first phase corresponding to the LTD reactions occurring between approximately 215-330 °C (Gou et al., 2022), with a phase transition of AP

from orthorhombic to cubic, while the second corresponding to the HTD reactions between approximately 330-420 °C (Kumar et al., 2018). The thermal decomposition of AP is a well-studied process and is often employed in rocket propellants and pyrotechnics. When heated to high temperatures, ammonium perchlorate decomposes, releasing gases and leaving behind solid residues. The decomposition reaction can be represented as follows (Wang et al., 2019):



This reaction illustrates the breakdown of ammonium perchlorate into water (H₂O), nitrogen gas (N₂), hydrogen chloride gas (HCl), and oxygen gas (O₂). The decomposition of ammonium perchlorate is highly exothermic, meaning it releases a significant amount of heat during the process (Becerra et al., 2011). This characteristic makes it valuable as an oxidiser in rocket propellants, where the liberated gases contribute to thrust generation. To analyse the thermal decomposition of AP, techniques like thermogravimetric analysis (TGA) and differential scanning calorimetry techniques (DSC) were employed to observe the thermal decomposition temperature of AP. Figure 2.7 shows the TGA and DSC curves of pure AP.

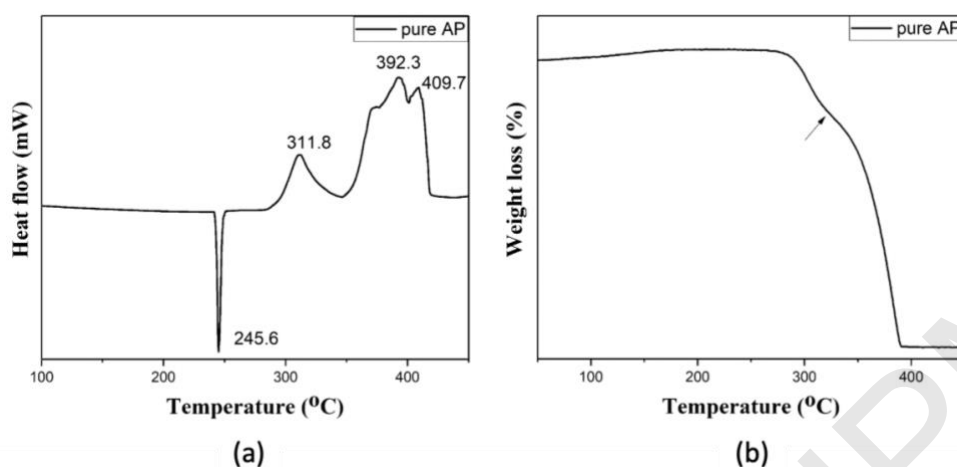


Figure 2.7: Typical (a) Differential scanning calorimetry (DSC) and (b) Thermogravimetric analysis (TGA) curve of ammonium perchlorate (AP)
(Source: Wang et al., 2019)

Catalysts have often been utilised in recent years to catalyse the thermal degradation process of AP to increase its performance. Metals and their oxides, carbon materials, and metal composite particles based on carbon materials are commonly used catalysts (El-Sayed et al., 2022). For example, Li et al. (2023) used a simple one-step method to prepare Ni/graphene nanocomposite under solvothermal conditions to catalytic thermal decomposition of AP, and they observed that the peak temperature of the high-temperature decomposition of AP decreased by 97.3 $^{\circ}\text{C}$. Hosseini et al. (2019) developed an efficient thermal decomposition of AP using Ni-Mn nanoparticles grown on three-dimensional nitrogen-doped graphene-based frameworks by the chemical co-reduction method. A study by Fertassi et al. (2023) showed the use of graphene (G)/CuO and Al/G/CuO composites as potential catalysts for the thermal decomposition of AP, reducing the high-temperature decomposition from 432 to 325 $^{\circ}\text{C}$. Nanosized metal copper is

often utilised to catalyse the thermal degradation of AP due to its tiny particle size, large specific surface area, and more reactive centres (Akbi et al., 2022).

2.5.3 Thermal Decomposition Principle of Ammonium Perchlorate in Composite Solid Propellant (CSP) Combustion Process

The oxidiser mass in the CSP generally constitutes 70-86 wt.% of the entire weight of the propellant. The oxidiser is the primary ingredient in the formulation of propellant, and hence, its decomposition plays a crucial part in the whole combustion process of the propellant. The interaction first occurs at the interface between the AP and fuel-binder, forming the main flame (Becerra et al., 2011). This results in heat release through convective and conductive processes, which promotes an increase in temperature to aid in the pyrolysis of fuel (Zhou et al., 2020). The disintegrated products release vapours that manifest as a diffusion flame rich in oxidisers. The form and temperature of flames are determined by the pace at which fuel vapours diffuse into oxidiser breakdown products. Combustion reactions occur rapidly inside the gaseous mixture, surpassing the diffusion rate (Khichar et al., 2019). The elucidation of the intricate chemical processes involved in the thorough combustion of propellant within a rocket engine, occurring under intense exothermic circumstances and elevated chamber pressure, is an exceedingly intricate matter. The understanding of the main combustion processes has been significantly improved through systematic studies conducted in the past on individual propellant ingredients and their mixtures under various operating conditions, ranging from sub-atmospheric to high chamber pressure conditions of the solid rocket motor. The use of precise analytical instruments

and advanced sensors has contributed significantly to obtaining data about quick thermolysis reactions, the high-temperature response of key products, and the related dissociation and recombination processes, as mentioned in the next section.

The thermal analysis data of AP obtained from DSC/TGA indicates that sublimation is the primary principle controlling AP degradation. Previous reports have suggested that sublimation has little impact under normal atmospheric pressure, but its significance grows as pressure decreases. An alternate situation arises when the pressure exceeds the surrounding environment, as in the rocket combustion process. Previous research by Chen et al. (2018), which performed AP decomposition at around 5 MPa in a nitrogen environment, determined that the HTD peak exhibits a downward change in temperature as pressure increases. The presence of N_2 was identified as the cause for this discovery, as it considerably facilitates the gas phase interaction between NH_3 and $HClO_4$. Several research studies have been conducted to understand the AP decomposition process better. Manash et al. (2019), El-Sayed et al. (2022), and Li et al. (2023) provide detailed explanations of the process of AP thermal degradation. Several principles have been presented, but the issue is still being debated. Two theories of the AP decomposition process, which are the electron transfer principle and the proton transfer principle, clearly describe how AP decomposes, and the details of each process will be elaborated on in the following subsection.

2.5.3.1 Electron Transfer Principle in The Thermal Decomposition of Ammonium Perchlorate

According to the reaction mechanism as in Kechit et al. (2021), decomposition occurs due to electron transfer from anion to cation:



Given the reduced distance between ions, there is an increased probability of electron realisation. Consequently, not only ammonium ions located in interstices but also all ammonium ions are considered excellent electron acceptors (Fertassi et al., 2023). Following electron absorption, the ammonium radical disintegrated into ammonia and hydrogen atoms:



Hydrogen migrates over the lattice. Electron migrates precisely in the same manner over the anion sublattice:



HClO₄ is generated because of the interaction of the ClO₄ radical with H. It might keep interacting with H:

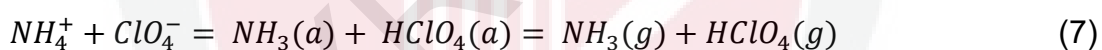


The ClO₃ radical acts as an electron trap, undergoing conversion into the ClO₃ ion upon capturing an electron. This is followed by the potential breakdown and interaction of the chlorite ion and ClO₄ radical with NH₄ ions, among others (Akbi et al., 2022). Such interactions yield secondary products, notably chlorine, nitrogen dioxide (NO₂), and water, highlighting the significance of

contact in product formation. An et al. (2022) delve into electron transitions within the context of energy band theory, specifically the transition of an electron from the valence band to the conduction band. Given that AP behaves as a typical dielectric, the process cannot be sustained by electron transfer at low temperatures of thermal disintegration due to its low likelihood (Kou et al., 2024). This effectively eliminates the idea of an electron transfer mechanism. Meanwhile, Farhadi Abkanar et al. (2020) have identified ammonia and perchloric acid as the primary products in their studies, suggesting that proton transfer is the major step of the thermal degradation of AP.

2.5.3.2 Proton Transfer Principle in The Thermal Decomposition of Ammonium Perchlorate

The thermal breakdown of the AP technique may be stated as a variant of the proton process (Yudha et al., 2021).



In the initial stage of the thermal degradation process of perchlorate ammonium (AP), a pair of ions within the AP lattice are engaged. This is followed by Stage II, which is the breakdown stage, which begins with proton transfer from the NH_4 cation to the ClO_4 anion via molecular complex, leading to their decomposition into ammonia and perchloric acid in Stage III. The resulting NH_3 and $HClO_4$ molecules either react in the adsorbed layer on the surface of perchlorate or desorb and sublime into the gas phase. At low temperatures, specifically around 350 °C, rapid reactions occur in the gas phase between NH_3 and $HClO_4$, producing side products such as O_2 , N_2O ,

Cl_2 , NO , and H_2O (Varghese et al., 2017). A critical aspect of AP's thermal degradation is that it occurs within pores under the surface at the micrometres scale, distinguishing it from mere sublimation. Milekhin et al. (2019) stated that during the adsorption process, perchloric acid desorbs more rapidly than ammonia, leading to incomplete oxidation of ammonia and creating a saturated NH_3 atmosphere. As a result, this slows the high-temperature breakdown and results in partial transformation. The second exothermic breakdown stage produces NO , O_2 , Cl_2 , and H_2O in the gas phase. In this circumstance, the activities occurring on the crystal's surface play the most crucial role: ammonia and chloric acid adsorption and desorption; hence, the importance of the fundamental processes associated with proton transfer rises (Tolmachoff et al., 2022).

2.5.4 Combustion By-Products of Ammonium Perchlorate in Solid Propellant Rockets Combustion Process

The previous section highlighted that the combustion of ammonium perchlorate (NH_4ClO_4) primarily yields water vapour (H_2O), nitrogen gas (N_2), hydrogen chloride gas (HCl), and oxygen gas (O_2). These gases are the typical products released during the combustion of ammonium perchlorate, and they contribute to the overall thrust and energy release in applications such as rocket propulsion (Dong et al., 2022). For more than 60 years, composite propellants based on ammonium perchlorate (AP, NH_4ClO_4) and aluminium (Al) have been widely used for both military and commercial purposes (Dalinger et al., 2018). Nonetheless, they pose environmental concerns in three major areas: (i) ground-based impacts, including groundwater

contamination and accidents due to improper handling and processing propellant; (ii) atmospheric impacts resulting from the interaction of exhaust combustion products with the surrounding atmosphere, including the ozone layer, and (iii) biological impacts encompassing propellant toxicity and corrosiveness (Nosseir et al., 2021). Additionally, the decomposition of AP during the combustion process of CSP, as shown in Figure 2.8, is known to impair thyroid gland function. Environmental pollution from AP-based propellants is marked by hydrochloric acid (HCl) release into the exhaust, contributing to significant environmental concerns. Furthermore, whilst aluminium compounds such as aluminium oxide (Al_2O_3) are not considered dangerous, their discharge as tiny particles as an aerosol may deleteriously affect humans, animals, and plants (Vellaisamy et al., 2020). The details of the effect of HCl on the environment will be discussed in a subsequent chapter.

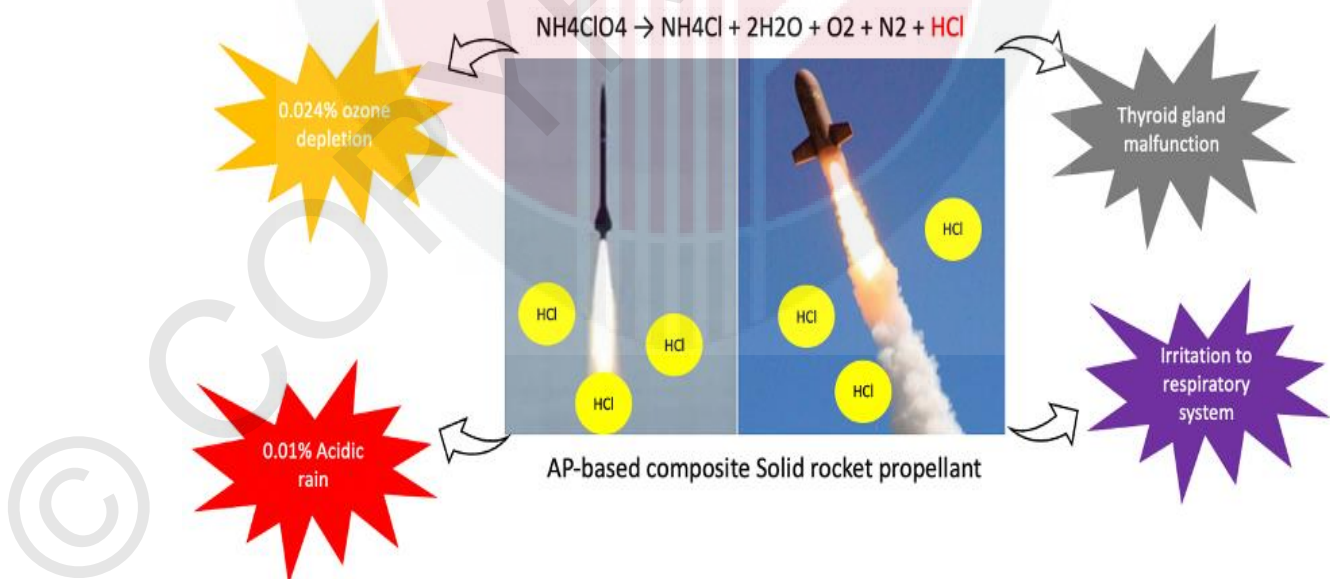


Figure 2.8: Ammonium perchlorate (AP) and its combustion products affect the environment

2.6 Potassium Permanganate (KMnO_4) as a Strong Oxidising Agent in Dual Oxidiser System of AP-Based CSP

2.6.1 Physical and Chemical Properties of Potassium Permanganate

Potassium permanganate (KMnO_4) is a crystalline solid that is violet in colour. The chemical compound potassium permanganate is made up of potassium (K), manganese (Mn), and oxygen (O), as indicated by its chemical formula, KMnO_4 . This chemical compound forms dark purple crystals or granules that, when dissolved in water, create a vivid pink or purple solution. Although it is non-combustible, KMnO_4 accelerates the burning of flammable materials and exhibits unique physical properties. KMnO_4 typically appears as a dark purple, almost black, crystalline solid, as illustrated in Figure 2.9. The crystals have a characteristic prismatic or rod-like structure. It also displays hygroscopic qualities, absorbing moisture from the air, which can lead to the crystals dissolving over time (Piezer et al., 2021). In general, KMnO_4 is stable when stored in dry conditions but can decompose in the presence of reducing agents, strong acids, or organic materials. Moreover, it is sometimes called by its common name, Condy's crystals (Kashif et al., 2021).



Figure 2.9: Physical structure of potassium permanganate (KMnO_4)
(Source: Wu et al., 2019)

One of its principal activities is as an oxidising agent, which means it can facilitate chemical reactions by receiving electrons from other compounds. Its vibrant purple colour is visually pleasing and serves as a valuable signal of its presence in solutions (Becerra et al., 2011). KMnO_4 is a versatile chemical compound with numerous applications, including water treatment and medical use, as well as the chemical industry and environmental cleanup (Álvarez-Hernández et al., 2019). Table 2.9 revealed the chemical properties of KMnO_4 . Its oxidising capabilities make it indispensable in a variety of fields.

Table 2.9: Chemical properties of potassium permanganate (KMnO_4)

Parameter	Value
Chemical formula	KMnO_4
Chemical structure	
Molecular weight	158.034 g/mol
Density	2.7 g/cm ³
Reaction with reducing agent	Potassium permanganate reacts vigorously with reducing agents.
Disproportionation Reaction	Potassium permanganate can undergo disproportionation reactions, where it simultaneously oxidises and reduces. For example, permanganate can disproportionate to form manganese dioxide (MnO_2) and manganate ions in alkaline solutions.
Melting point	240 °C
Compatibility	Ammonium perchlorate is often combined with powdered metals (such as powdered aluminium) as a fuel to enhance its performance in rocket propellants.

(Source: Álvarez-Hernández et al., 2019)

However, it is critical to handle KMnO_4 with caution and follow safety precautions to guarantee its safe and effective use. Understanding its applications and qualities can help professionals and hobbyists alike realise its full potential. Based on the reported study by Lide et al. (2004), some of the current applications of KMnO_4 are shown in Figure 2.10.

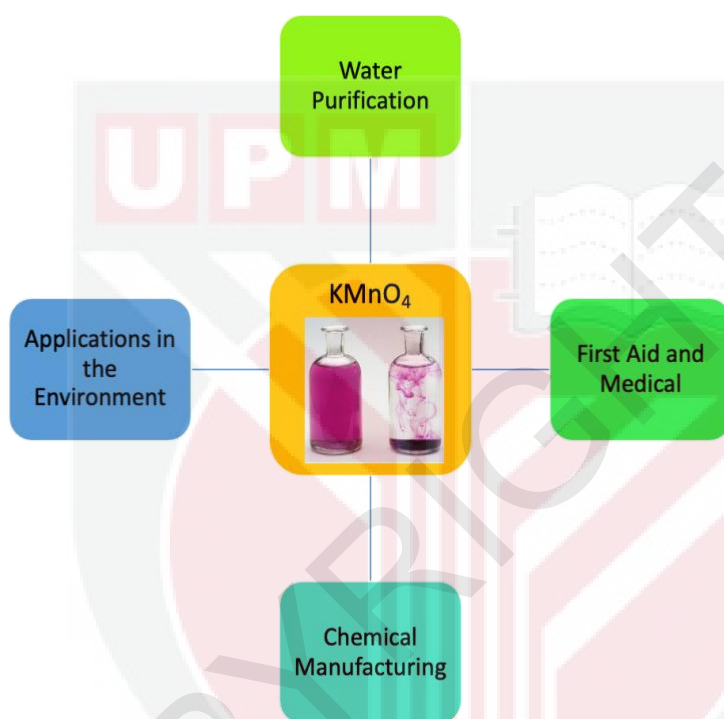
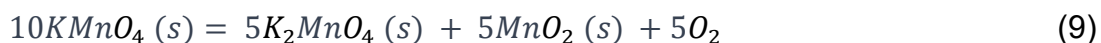


Figure 2.10: Application of potassium permanganate (KMnO_4)

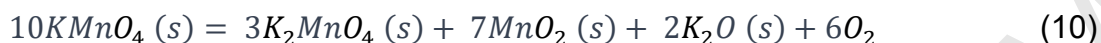
2.6.2 Thermal Decomposition Properties of Potassium Permanganate

Numerous investigations have been conducted on the thermal decomposition of potassium permanganate (KMnO_4). Almost all authoritative laboratories in the world, including the authors Rudorf et al. (1901), Hinshelwood et al. (1921), and Khan et al. (2012), which have researched the mechanism and kinetics of its breakdown in the 190 years since the first publication by Chevillot et al.

(1817) Initially, the resulting reaction has been represented by either the scheme:



which is equivalent to the scheme of reaction or by the scheme:



Over a century ago, Rudolf et al. (1901) proposed that the distinction between these two systems is primarily based on the varying ratios of solid products and free oxygen, with the latter ranging from 10 to 12 wt%. The thermal decomposition of $KMnO_4$ involves the breakdown of the compound into different products through the application of heat (Aprilliani et al., 2018). Finally, the general thermal decomposition reaction for $KMnO_4$ has been finalised and evaluated as can be represented as follows:



In this reaction, potassium permanganate ($2KMnO_4$) undergoes decomposition to yield potassium manganate (K_2MnO_4) and oxygen gas (O_2) with the manganese within the permanganate ion undergoes a shift in oxidation state. It is important to note that the thermal decomposition of potassium permanganate typically requires relatively high temperatures (Svedin et al., 2023). The decomposition of $KMnO_4$ occurs at approximately 240°C (464°F), although the specific temperature for decomposition occurs may vary, but it is generally well above room temperature. Figure 2.11 shows the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of $KMnO_4$.

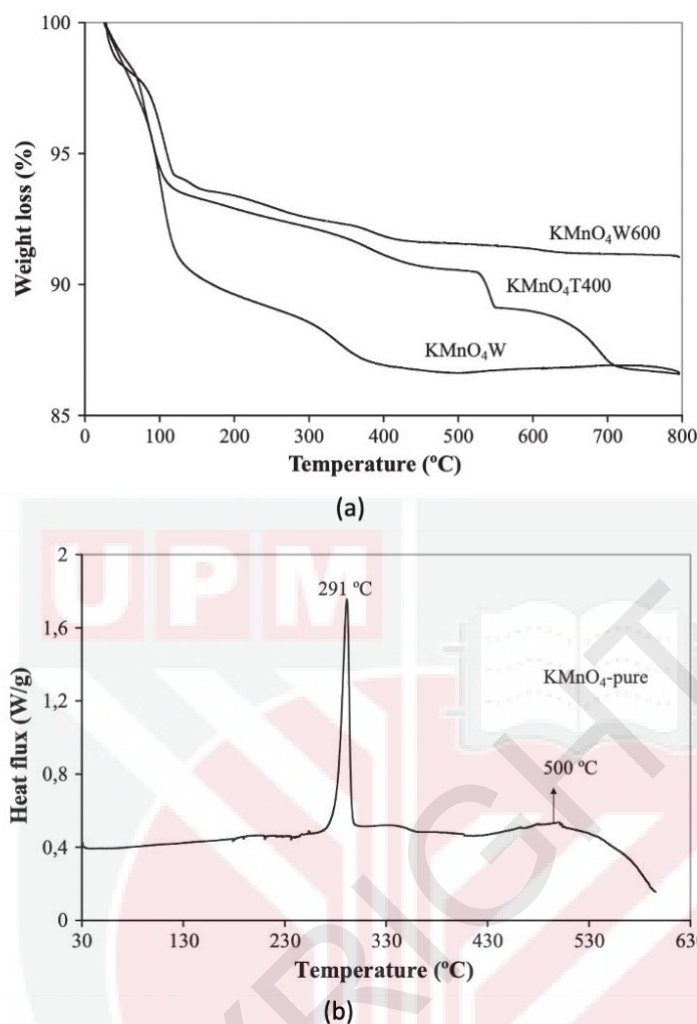


Figure 2.11: Thermal properties of potassium permanganate (KMnO_4) using (a) thermogravimetric analysis (TGA) under nitrogen atmosphere, (b) differential scanning calorimetry (DSC) under nitrogen atmosphere (Source: Becerra et al., 2011)

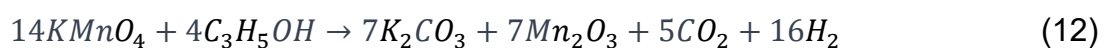
The research conducted by Bacerra et al. (2011) focuses on the thermal decomposition of KMnO_4 , analysing three distinct as depicted in Figure 2.11.

These samples include: (i) $\text{KMnO}_4\text{T400}$, where commercial KMnO_4 is calcined in air at 400 °C for 6 hours with a heating rate 10 °C/min; (ii) KMnO_4W , which is the $\text{KMnO}_4\text{T400}$ sample post-washed with distilled and deionised water to remove soluble salts (potassium manganate) formed during the calcination; and (iii) a subsequent calcination of the KMnO_4W sample at 600 °C for 6 hours

with a heating rate of 10 °C/min. The thermal gravimetric analysis (TGA) curves for each sample exhibit a consistent trend, reflective of the typical behaviour observed in the TGA of KMnO_4 . Factors such as catalysts, impurities, and specific reaction conditions can influence the decomposition reaction (Cai et al., 2020). Upon heating, KMnO_4 releases oxygen gas and undergoes a colour change. The release of oxygen is a characteristic feature of the thermal decomposition of many metal permanganates. Given its strong oxidising properties, caution is advised to mitigate safety risks when handling and heating KMnO_4 , especially at elevated temperatures (Ebrahimi et al., 2021).

2.6.3 Combustion Products of KMnO_4 as Propellant Oxidiser

Potassium permanganate (KMnO_4) can be used in combustion applications, particularly for fire-starting or emergency fire lighting. When potassium permanganate contacts with certain reducing agents, it can undergo an exothermic reaction, producing heat and igniting a fire (Polis et al., 2022). Glycerin, or another suitable organic material, often serves as the reducing agent in such applications (Zhang et al., 2024). In the context of fire-starting or combustion scenarios, glycerin is commonly used as the reducing agent. The chemical reaction between KMnO_4 and glycerin can be represented as follows:



In this reaction, glycerin ($\text{C}_3\text{H}_5\text{OH}$) serves as the reducing agent and undergoes oxidation. Concurrently, KMnO_4 undergoes reduction, resulting in

manganese dioxide (Mn₂O₃) formation. This process releases a considerable amount of heat, leading to the onset of combustion (Najser et al., 2022). Potassium permanganate (KMnO₄) finds applications in solid fuel applications, particularly within pyrotechnics or as an ignition aid in emergencies. This compound is known for its potent oxidising properties, and when incorporated into solid fuel formulations, it can act as an oxidiser to enhance combustion (Zhai et al., 2021). In some solid fuel formulations, KMnO₄ is blended with a fuel source and additional components to create a mixture that, upon ignition, releases heat and gas. This can be useful in applications such as emergency fire starters, signal flares, or other pyrotechnic devices (Mutrakulcharoen et al., 2021). The overall reaction involves the oxidation of the fuel source by KMnO₄. A simplified example of a reaction using KMnO₄ in a solid fuel composition (Boulangé et al., 2019):



The fuel in this reaction might consist of organic material such as sugars or other combustible substances. Recently, sugars, including sucrose, fructose, and sorbitol, have been utilised to formulate solid rocket propellants as sounding hobby rockets. These sugars serve as the fuel component within the propellant mixture (McClain et al., 2021). Commonly paired oxidisers with these sugars include potassium nitrate and sodium nitrate, leading to their designation as sugar-based solid propellant rockets (Garino et al., 2021). Based on the review conducted, there is a lack of data concerning the application of KMnO₄ in sugar-based solid rocket propellants. The same goes for composite solid propellant (CSP), where KMnO₄ is not a common

ingredient in the formulations. Typically, the oxidisers used in solid rocket propellants are either ammonium perchlorate (AP) or ammonium nitrate (AN), with the fuel consisting of either powdered metal or a hydrocarbon-based material. However, due to its strong oxidising properties and ability to produce non-toxic gas as combustion by-products, KMnO_4 can be integrated into AP-based formulation systems. The potential of this novelty will be discussed in the next chapter. Figure 2.12 shows the hypothesis effect of KMnO_4 on the decomposition mechanism of AP, as suggested in this research.

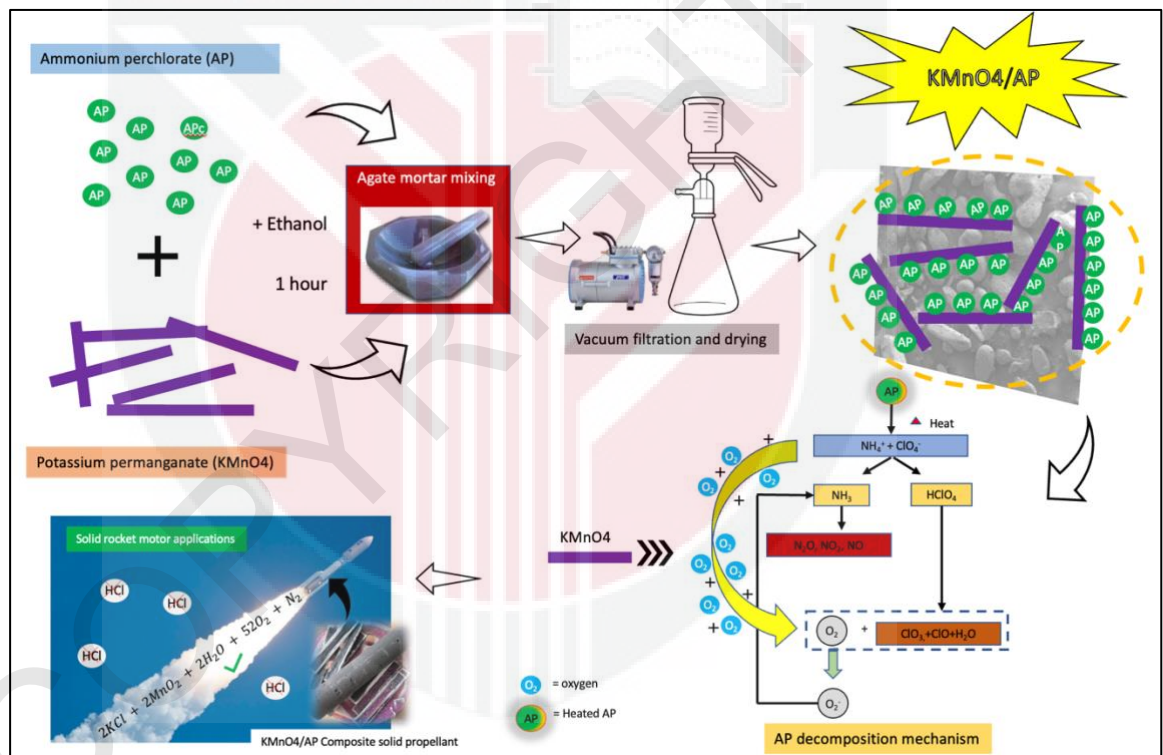


Figure 2.12: Hypothesis of KMnO_4/AP composite solid propellant effect on the combustion by-products in solid rocket motor application

2.7 Hydrochloric Acid Gas (HCl) as Combustion By-Products of AP-Based CSP and its Effect on The Environment

Hydrochloric acid (HCl) gas is a colourless, corrosive gas with a stifling, unpleasant odour. It is very soluble in water, and it reacts to generate hydrochloric acid. In the atmosphere, HCl can exist in both gaseous and aerosol forms, and its partitioning between the two is temperature- and humidity-dependent (Trokhimovskiy et al., 2021). Lower ambient temperatures and higher relative humidity in the atmosphere facilitate aerosol formation. The abundance of droplet nucleation sites in rocket exhaust clouds further influences the gas-liquid balance. Owing to its high water solubility, inhaled HCl rapidly dissociates upon contact with the moisture in the upper respiratory tract (Ji et al., 2020).

HCl can be made in a variety of ways. In the United States (90%), the vast majority of HCl production is a byproduct of various chlorination procedures (Bommaraju 2007), while only 8% is directly synthesised from hydrogen gas (H_2) and chlorine gas (Cl_2). The combustion of chlorine-containing organic compounds produces HCl. HCl concentrations in combustion flue gas have been observed to reach 3,030 ppm on average (Sebacher et al., 1980). Naturally, HCl is present in volcanic gases, particularly in Mexico and South America, and it is possible that it was one of the gases in the earth's original atmosphere (Ren et al., 2019). From natural sources, sea salt-derived HCl is the primary source of tropospheric HCl (Mehr et al., 2020). Combustion of fossil fuels (especially coal) is the most common anthropogenic source of ambient HCl concentrations, measured in the range of 0.5-7.6 ppm (Pye et al.,

2020). In areas near sources of HCl from combustion, (Ekezie et al., 2019) estimated the maximum HCl concentrations to be in the range of 20-30 ppm. The physical and chemical properties of HCl can be seen in Table 2.10.

Table 2.10: Physical and chemical properties of hydrochloric acid (HCl)

CAS No.	7647-01-0
Molecular formula	HCl
Molecular weight	36.47
Chemical name	Hydrogen chloride
Synonyms	Muriatic acid, spirits of salt, chlorhydric acid, hydrochloric acid gas
Physical state	Gas
Boiling point	-84.9°C
Melting point	-144.8°C
Vapor density	1.26 (air = 1.0)
Vapor pressure	40 mm Hg at 17.8°C
Solubility	Highly soluble in water, forming hydrochloric acid (82.3 g/100 g of water at 0°C)
Colour	Colourless as a gas

(Source: Alamiery et al., 2021)

In a rocket, HCl is formed during the combustion of composite solid propellant (CSP) rockets containing ammonium perchlorate (AP). The primary combustion reaction of AP-producing HCl gas is as follows:



For three different rocket types, the HCl concentration in the exhaust of a solid propellant rocket utilising AP as an oxidiser was calculated to be between 18.31 and 19.41 grams of HCl per 100 grams of propellant consumed (Terry et al., 2016). Pellett et al. (1983) reported that the exhaust from a solid rocket fuel space shuttle launch contained 60 tons of HCl. In the case of eight Titan III rockets, the peak HCl concentrations in altitude-stabilized exhaust clouds

ranged from 25 to 0.5 ppm over 3-300 min. Partitioning experiments revealed that the total HCl produced by a US space shuttle launch was primarily aerosol form; however, due to rapid dissipation, the gaseous phase became the dominant condition within several minutes post-launch (Chalghoum et al., 2020). Except in high humidity conditions (over 90%), the gaseous phase of HCl would predominate at equilibrium under the unpolluted tropospheric HCl concentrations of less than 1 ppm (Trokhimovskiy et al., 2021).

2.7.1 Limiting Allowable Concentration of Hydrochloric (HCl) Gas In Environmental Aspect Condition

For the combustion of perchlorate-based formulations, up to 20 - 25% wt. of the primary product is HCl, which poses a significant threat to the ozone layer (Ríos et al., 2019). Furthermore, when rockets are launched or discarded on Earth's surface, vegetation suffers over a large area which limits the allowable concentration (LAC) of HCl is 5 mg/m³ (Kuzmin et al., 2015). Primarily, HCl precipitates directly above the launch site, covering an area of 12 hectares. However, its fallout has been observed as far as 78 km away, with concentrations in the neighbouring regions potentially exceeding the LAC by a factor of 20 (Abada et al., 2020). This value exceeds the safety levels specified in Table 1.9 and is classified as a hazard based on acute exposure guideline levels (AEGL) in Table 2.11. Other hazardous combustion products of chlorine-containing formulations include highly toxic dioxins (Chen et al., 2019).

Table 2.11: Acute exposure guideline level (AEGL) value for hydrochloric acid gas (HCl) (ppm [mg/m³])

Classification	10 min (ppm)	30 min (ppm)	1 hr (ppm)	4 hrs (ppm)	8 hrs (ppm)	End Point (Reference)
AEGL-1 (Non-Disabling)	1.8	1.8	1.8	1.8	1.8	NOAEL in exercising asthmatic subjects (Stevens et al., 1992)
AEGL-2 (Disabling)	100	43	22	11	11	Mouse RD50 (Barrow et al., 1977)
(Lethal)	-937	-313	-155	-39	-39	NOEL for death from I-h rat LC50 (Wohlslagel et al., 1976; Vernot et al., 1977; histopathology in rats (Stavert et al., 1991))

Abbreviations: LC50, concentration lethal to 50% of subjects; mg/m³, milligrams per cubic metre; NOAEL, no-observed-adverse-effect level; NOEL, no-observed-effect level; ppm, parts per million; RD50, concentration expected to cause a 50% decrease in respiratory rate.

Table 2.12: Effects of hydrogen chloride (HCl) concentration on human respiratory health

HCl exposure limits (ppm)	Health effects
> 5	Coughing
35	Throat irritation occurs after only a short time.
> 35	Severe breathing difficulties and skin inflammation or burns
10-50	Maximum level that can be sustained for several hours
> 100	Swelling of the lungs and often throat spasms
50-1000	Maximum possible exposure: 1 hr
1000-2000	Very dangerous, even for a very short exposure

(Source: Lide et al., 2004; Baxter et al., 2010)

AP is suspected to affect thyroid gland function (Yadav et al., 2021). The environmental pollution from AP-based propellants primarily stems from the emissions of HCl as an exhaust product. A major space vehicle launch produces around 580 tonnes of HCl and hazardous heavy metal oxides, which damage the stratosphere, land, and water sources (Sinditskii et al., 2015). The launch of six Titan-class spacecraft might result in 0.024% ozone depletion and 0.01% acidic rain in the stratosphere (Trache et al., 2017). Thus, research on finding new or promising materials to replace conventional composition, especially AP, must be done to mitigate environmental impact, protect human health, conserve resources, comply with regulations, enhance public perception, and ensure the long-term viability of space exploration.

2.8 Hydrochloric (HCl) Gas Reduction Efforts in AP-Based Composite Solid Propellant Combustion By-Products

In general, the never-ending quest for better propellant systems necessitates increased performance levels in terms of burning rate and specific impulse (I_{sp}), along with maintaining acceptable mechanical properties, ageing characteristics, cost-effectiveness, processability, safety, storage, and environmental sustainability. New solid rocket formulations should match or exceed the qualities of current AP/Al/HTPB-based systems (Kohga et al., 2019). Furthermore, the military sector requires the development of innovative, smokeless, low-signature, and environmentally friendly formulations (Kumar et al., 2018). In this regard, various modern laboratories are investigating a variety of novel substances as potential candidates for industrial uses. Although many high-energy density materials have been

identified to overcome the shortcomings, the majority remain impractical for short-term use due to a variety of severe difficulties in large-scale manufacture, ground processing, personnel safety at various stages, handling and transportation safety, shock sensitivity, prolonged storage, and cost considerations (Sims et al., 2022). Work is being done globally every day, yet no integrated vehicle designs currently use these innovative propellant compounds and compositions. Figure 2.13 illustrates the current efforts to find replacement materials or innovations for AP as an oxidiser in the CSP system.

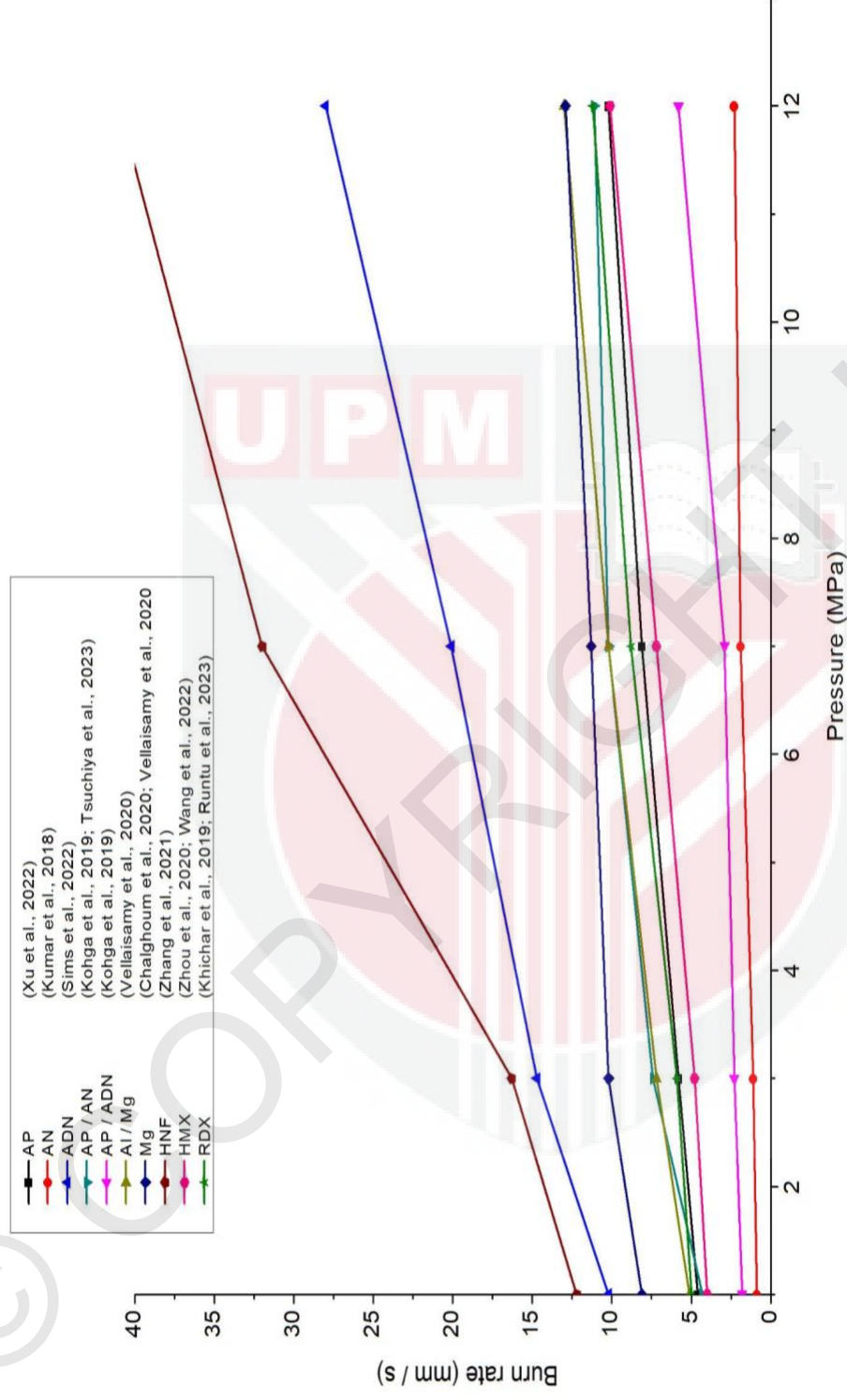


Figure 2.13: Research finding on the currently developed promising materials for replacing ammonium perchlorate (AP) as composite solid propellants (CSP) oxidiser and additives in reducing HCl as combustion by-products with their burn rate performance

Following a brief historical review, exploring contemporary components such as solid oxidisers, metal fuels, and binder systems has revealed many interesting developments. Some alternative oxidisers that have been explored for solid rocket propellants include ammonium nitrate (AN), ammonium dinitramide (ADN), hydroxylammonium nitrate (HAN), and various metal oxides. For example, Kohga et al. (2019) synthesised a novel dual oxidiser by combining AP with AN to reduce the HCl gas emissions in rocket motor exhaust, while Chen et al. (2023) explored using ADN as a replacement for the AP oxidiser in CSP systems. However, these replacements aim to reduce AP usage without providing experimental data on the resulting HCl concentration value as a by-product. Among the oxidisers, ADN-based systems are receiving special attention to progress the existing state-of-the-art in solid propellant formulations (Alamiery et al., 2021), despite the fact that ADN's fundamental properties such as physical, chemical, mechanical, ballistic, and so on, are not yet ideal for solid rocket propulsion, especially for space applications. Dual-oxidiser systems, such as ADN+AN or ADN+AP, combined with dual-metal fuels and either inert or energetic binders, have shown potential for improving solid rocket propulsion (Xu et al., 2022). The first type of formulation is more prone to have a lower environmental effect by being a "green" oxidiser with no HCl generation at the expense of a slightly lower specific impulse (Isp) value. In contrast, the second is more prone to maximising mission performance by increasing Isp at the expense of minor HCl production. However, these and other potential suggestions are far from practical applications in flight (Yeh et al., 2021). Today, possible candidates for primary oxidisers for solid rocket propulsion include AN, AP, HNF

Hydrazinium Nitroformate (HNF), ADN, and HNIW 2,4,6,8,10,12 Hexaazaisowurtzitane (HNIW). Furthermore, hexogen (RDX) and octogen (HMX) are frequently utilised as secondary oxidisers in high-performance military propulsion missions (DeLuca et al., 2018). While AN and AP are well-known solid inorganic oxidisers employed for decades at all levels, RDX and HMX are solid organic explosives. HNF and ADN, on the other hand, are relatively new solid energetic materials with high energy content, chlorine-free formulation, and smokeless exhausts. Theoretically, any of these could replace AP (Manash et al., 2019).

Research done by Unni et al. (2020) has shown that incorporating metal additives into composite propellants significantly reduces the percentage of HCl in exhaust gases produced during combustion by more than 95%. A theoretical performance study performed by Pal et al. (2019) has demonstrated that binary metal combinations exhibit higher Isp than solid propellants consisting only of pure metals. Further experimental analysis of the combustion properties of metal additives, mainly focusing on flame morphology, suggests that binary metal mixtures exhibit improved burning characteristics (Mason et al., 2019). This improvement is attributed to an increased distance between the reaction zone and the liquid metal, leading to a higher burn rate. The utilisation of binary metal mixtures is advantageous because it necessitates a smaller ignition source due to the formation of a eutectic alloy. The investigators made by Terry et al. (2016) reported using an additional method to enhance the combustion rate of metal additions. This involved employing a pseudo-alloy composed of metals that are not mutually

soluble. Specifically, high-melting-point metals were embedded inside a matrix of low-melting-point metals (Li-Be) (Lawrence et al., 2019). However, a critical and comprehensive investigation into the effects of metal incorporation, especially concerning the increase in burn rate and reduction of HCl emissions when metals are added to conventional AP solid propellants, remains lacking. This gap, highlighted by Chalghoum et al. (2020), points to the need for further study on the mechanical properties vital for developing new CSP formulations. Experimental findings work conducted by Vellaisamy et al. (2020) reported that adding metal additives, specifically Al-Mg at 15%, enhances the burn rate and minimises the HCl concentration by 51%. Currently, the challenges lie in addressing HCl emissions without compromising the performance of solid rockets. Figure 2.14 revealed the findings based on the literature on adding metal additives to reduce HCl concentration as combustion by-products with burn rate properties.

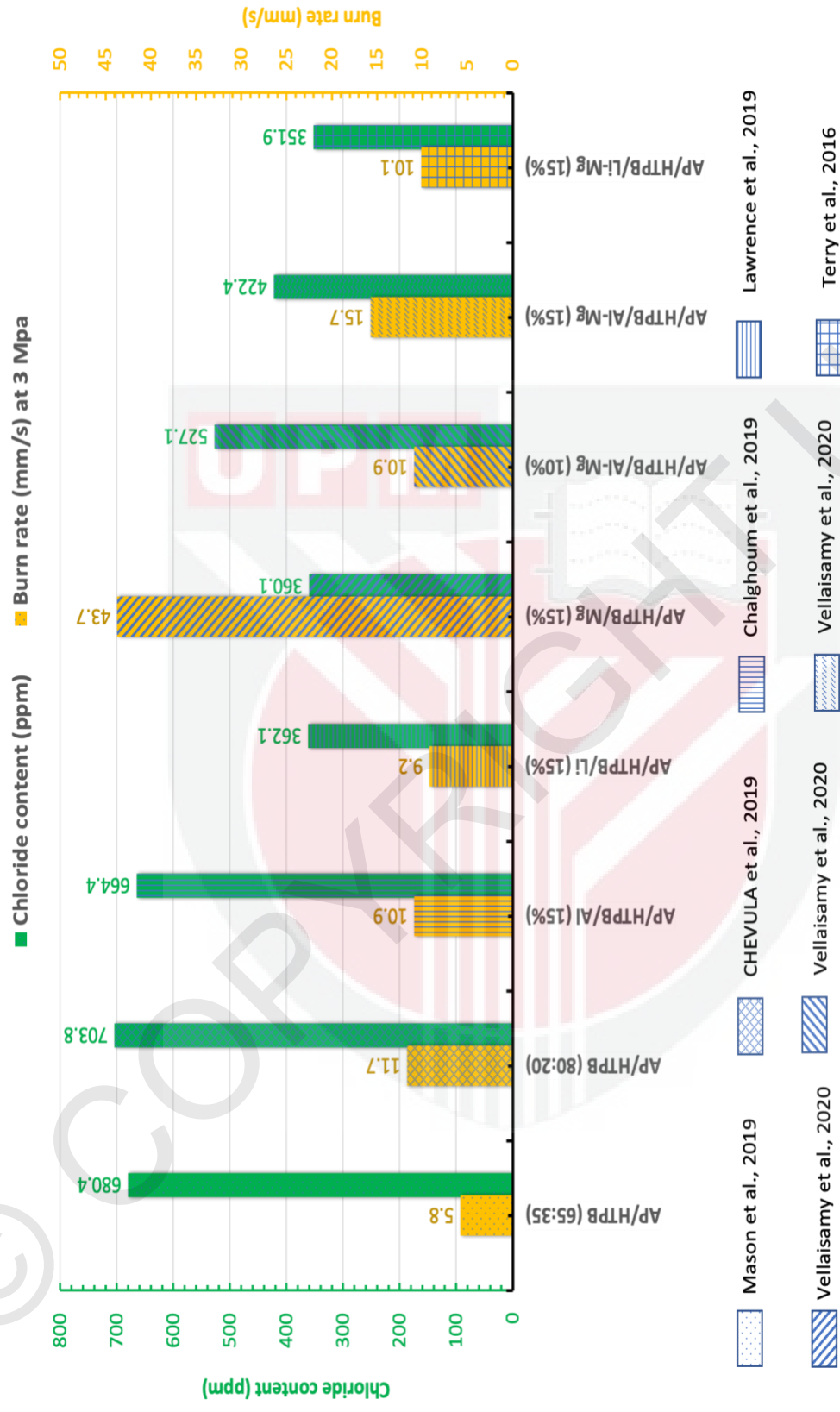


Figure 2.14: Efforts on HCl reduction of AP-based CSP based on literature findings

2.9 Tensile Properties and Behaviour of AP-Based Composite Solid Propellant Grain

As military technology advances, the demand for missiles with enhanced performance capabilities grows. Additionally, it increases the need for improved capabilities of SRM to meet the dual objectives of adhering to safety margin standards and ensuring performance improvements. This is particularly crucial for tactical missiles, which are subject to strict criteria for the structural integrity of solid propellants (Gong et al., 2020). Research by Ashish et al. (2019) and Lysien et al. (2021) indicates that igniting SRM requires a few tens of seconds to generate high internal pressure. However, conventional research conducted at low strain rates fails to accurately represent the significant disparities in the mechanical characteristics of solid propellants under varying strain rates. Khan et al. (2012) conducted theoretical and experimental studies on strain rates to derive constitutive equations for solid propellant ignition in SRM. Furthermore, Wang et al. (2016) emphasised the importance of considering the tensile properties of the CSP grain when developing novel properties. For example, the development of novel catalysts for burn rate enhancement is perfect for propellant combustion performance. However, if the propellant grain does not meet the minimum tensile strength required for the CSP, the whole rocket motor system will fail because the solid grain cannot sustain the high pressure in the rocket motor (Singh et al., 2019). According to Bhowmik et al. (2017), some of the important tensile properties in CSP are safety and reliability, performance optimisation, ease of material selection, ageing and storage, and failure analysis.

Typically, a solid rocket motor operates effectively under various loading conditions, including temperature fluctuations, launch pressure, transportation vibrations, and others (Wibowo et al., 2018). Given these operational circumstances, it is crucial to comprehend and forecast the material response of the solid propellants under different situations. The composite formulation must withstand several production, shipping, storage, and operating cycles when composite propellants are exposed to heat and mechanical stresses without protection (Jiang et al., 2019). From a mechanical perspective, the solid propellant may be seen as a composite material reinforced by particulates, where the matrix is made of HTPB, and the reinforcing material is AP. Previous research by Pauline et al. (2020) has shown that this solid propellant has a high level of viscoelasticity, perhaps with the presence of the Mullins effect. Additionally, there is a debonding phenomenon between the reinforcing materials and the matrix, as shown in experimental works conducted by (Kumar et al., 2019). The Mullins effect is a well-documented phenomenon observed in most polymer materials. It occurs when the deformation of these materials leads to the loosening and breaking of polymer chains and the breaking of cross-links between the chains. The macroscopic manifestation of the Mullins effect may be detected in a cyclic loading scenario. The first loading curve obtained with the pristine material will have a greater magnitude than the subsequent reloading curves seen after each unloading cycle (Kaur et al., 2020). Mechanical failure refers to either a reduction in lifespan or a total collapse of the system. The mechanical characteristics and lifespan of the composite propellant are primarily assessed by applying uniaxial tensile testing (Chaturvedi et al., 2019). The selection of propellant

formulation is crucial for achieving optimal performance parameters, ballistic characteristics, and mechanical qualities in composite propellant design.

Hydroxyl-terminated polybutadiene (HTPB) is the predominant binder due to its advantageous mechanical characteristics. Recent research indicates that using additives like ammonium perchlorate (AP) in HTPB can substantially improve tensile strength. Zhang et al. (2021) documented a 46.2% enhancement in tensile strength by utilising chemically modified HTPB in composite propellants, underscoring the significance of binder modification in improving mechanical properties. The integration of polydopamine (PDA) coated AP particles has demonstrated an increase in the tensile strength of propellants from 1.2 to 1.8 MPa, suggesting that surface modifications can enhance the adhesion between AP and the binder, thus improving the overall mechanical integrity of the propellant (Yang, 2023).

AP particles, especially in size and shape, significantly influence the tensile strength of solid propellants. Jain et al. (2009) emphasised that propellants' rheological and viscoelastic characteristics are greatly affected by the shape of solid components, such as AP. Smaller and more uniform particles generally provide a more homogeneous mixture, resulting in enhanced mechanical characteristics. The integration of nanoparticles, specifically nano-sized chromium oxide, has demonstrated an improvement in the tensile strength and elastic modulus of HTPB/AP/Al-based propellants, highlighting the influence of particle size on mechanical performance (Kshirsagar et al., 2016).

2.9.1 Tensile Fracture Behaviour of Composite Solid Propellant Grain

The tensile fracture behaviour of ammonium perchlorate (AP) and hydroxyl-terminated polybutadiene (HTPB) based solid propellants is rather complicated, depending on propellant microstructure, loading condition, and environmental factors such as temperature and strain rate. These behaviours should be investigated if solid propellants' performance and safety optimisation for practical application are aimed.

One of the predominant tensile fracture mechanisms for AP-HTPB base propellants involves the interaction, under tensile loading, between the AP particles and the HTPB binder. Under applied stress conditions, the growth of voids around the AP particles can occur to develop a dilatational response in addition to an axial strain response. Li et al. (2020) pointed out that such dilatation forms a key feature of the mechanical behaviour of solid propellants under tensile loading, which can be further decomposed into deviatoric and dilational responses. This shows that fracture is not just dependent on tensile strength but also on how the material deforms and accommodates the stress.

Fundamentally, the conditions of temperature and strain rate under which the propellant is tested determine largely the tensile fracture characteristics. Wang et al. (2015) carried out experiments which showed that HTPB propellants have a different fracture mechanism under low-temperature-high-strain-rate conditions. The test results showed that the propellant had greater brittleness at low temperatures while it became ductile at higher temperatures; this could affect the fracture surface morphology as observed under scanning electron

microscopy (SEM). Additionally, Li et al. (2021) conducted another study in which it was found that mechanical properties are closely related to the propellant mesoscopic structure, which means that improvement in microstructure will lead to an enhancement of tensile strength and fracture toughness.

The additives and modifications in the HTPB binder may further enhance the tensile fracture behaviour. For instance, Zhang et al. (2021) demonstrated that chemical modification of HTPB can lead to significant enhancements of these fundamental properties of mechanical concern-tensile strength and elongation-both crucial to propellant performance. These modifications can affect the fracture mechanisms, thus improving the bonding between AP and binder. The latter provides a reduced possibility for the initiation and propagation of cracks.

Although the stress distribution in solid rocket propellants during operation is not a straightforward uniaxial stress condition, the most performed test to determine the percentage of elongation, tensile strength, and Young's modulus is the uniaxial tensile test (Boshra et al., 2021). The acquired findings demonstrate the reproducibility and reliability of the propellant process. The experiment is conducted using a universal tensile testing machine, using a standard JANNAF type of dog bone sample (Zhang et al., 2018). The specimen is clamped inside the jaws of a Universal Testing Machine (UTM), and one of the jaws is let to move upwards until the specimen fails. The crosshead speed is appropriately chosen, and typically, a speed of 50 mm/min

is selected for explosive samples specifically for composite propellant. The stress/strain curve is recorded, and specialised software is used to extract the tensile strength, % elongation, and Young's modulus from the curve. Furthermore, experimental work conducted by Kim et al. (2019) shows that the sample's temperature condition influences the CSP's tensile strength. This study parameter will illustrate the CSP sample's actual behaviour in which the condition is the same as in the rocket motor when it is in operation (Pimont et al., 2019). The result from that experimental work reported that Young's modulus increases as temperature decreases, but the percentage elongation shows the opposite pattern.

Consequently, the Young's modulus of the CSP grain system should be modest, about 3-10 MPa (Pradhan et al., 2020). In contrast, free-standing grain should possess a high level of tensile strength and a low elongation percentage, resulting in a substantially greater Young's modulus (above 30 MPa) (Cegla et al., 2019). Typically, case-bonded motors, ranging from small to big, exhibit the following values for the tensile mode parameter as in Table 2.13.

Table 2.13: Tensile mode theoretical parameter constraints for composite solid propellant

Tensile strength	0.5 - 2 MPa
Initial modulus	2.5 - 5 MPa
Elongation (%)	> 30%

(Source: Ashish et al., 2019)

Tensile strength is the maximum tensile force a material can withstand before breaking, measured per unit cross-sectional area. The elongation (%) refers to the capacity of a material to stretch or deform before it reaches the point of failure. The stress/strain curve depicted in Figure 2.15 demonstrates the theoretical mechanical characteristics assessed during the uniaxial constant strain rate laboratory test (Tola et al., 2018). The maximum stress (σ) is utilised to establish the permissible stress level for the propellant, whilst the strain (ϵ) at maximum stress is employed to determine the allowable strain level (Kumar et al., 2019).

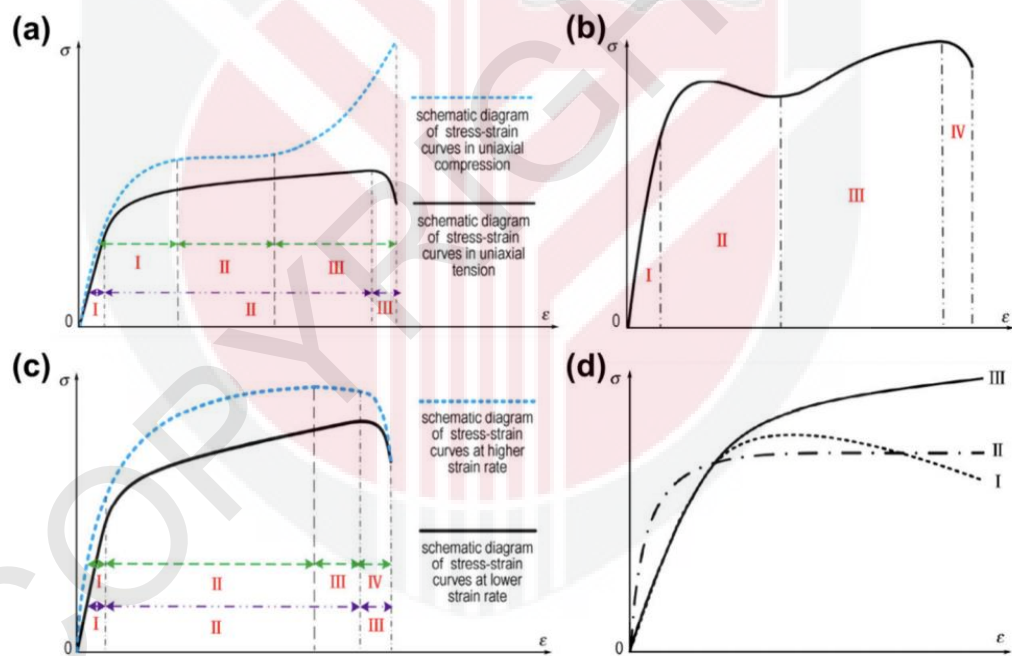


Figure 2.15: Stress-strain curves of composite solid propellants subjected to various loading conditions (a) Uniaxial compression, (b) Low-temperature quasi-static compression, (c) High-strain-rate compression, and (d) Low-temperature quasi-static uniaxial tension (Source: Wang et al., 2016)

Figure 2.15 displays stress-strain curves of composite solid propellants subjected to various loading conditions. These conditions include: (a) Uniaxial compression, which consists of three sections: I) linear elastic section, II) stress-hardening section, and III) failure instability section. Uniaxial tension also has three sections: I) linear elastic section, II) "dewetting" damage section, and III) failure section. (b) Low-temperature quasi-static compression has four sections: I) initial linear section, II) yield and strain-softening section, III) strain-strengthening section, and IV) failure section. (c) High-strain-rate compression has four sections: I) initial linear section, II) stress-hardening section, III) strain-softening section, and IV) failure section. Low-strain-rate compression has three sections: I) linear elastic section, II) stress-hardening section, and III) failure instability section. (d) Low-temperature quasi-static uniaxial tension, which has three factors dominating each section: I and II yield factor dominate, "dewetting" and poor interface bonding, curve shape showing tail dropping or plateau; III deformation factor dominates, good interface bonding, curve shape showing upward. The tensile stress-strain curve of a composite solid propellant can be divided into three distinct stages: a linear elastic section, a "dewetting" damage section, and a failure section (de Francqueville et al., 2021). On the other hand, the compressive stress-strain curve consists of a linear elastic section (I), a stress-hardening section (II), and a failure instability section (III), as shown in Figure 2.15 (a), Pal et al. (2019) proposed that the presence of a damaged area known as the "dewetting" suggests the development of tiny fractures in the solid propellant composite. These fissures cause the particles to separate from the matrix, resulting in a decrease in load-bearing capacity and a non-linear relationship between

stress and strain. Chandru et al. (2018) posited that the stress-hardening section corresponds to the plastic deformation resulting from macroscopic fractures inside the composite solid propellant.

2.10 Burn Rate Properties of AP-Based Composite Solid Propellants in The Combustion Process

The burning surface, burning rate, grain shape of the propellant, and other combustion characteristics determine the functioning and design of the rocket engine. The field of applied science that deals with studying these phenomena is referred to as internal ballistics. The regression surface of a solid propellant is a defining characteristic of its combustion process. The burning rate refers to the pace at which the flame front moves per unit of time, often measured perpendicular to the burning surface (Sreejith et al., 2021). This front is presumed to be regular and typically advances perpendicular to itself. This has been empirically confirmed (within the precision threshold of charred profile measurements) by halting the propellant combustion and inspecting the surface (Wang et al., 2022). The rate of regression, typically measured in centimetres per second (cm/s), millimetres per second (mm/s), or inches per second (in/s), refers to the speed at which burning occurs (Zamostianu et al., 2022). Figure 2.16 illustrates the alteration of the grain geometry by the depiction of consecutive burning surfaces, with a consistent time interval between each contour. This visualisation also depicts a two-dimensional grain, including a core cylindrical chamber. Besides, combustion starts over the whole extent of the central core, with the burning area moving away from the centre in a radial direction (shown at random moments t_1 , t_2 , t_3) (Jain et al.,

2019). It is essential to observe that the surface area that is on fire (shown by the length of the red lines in this diagram) is consistently growing. Information on the burning rate behaviour of the chosen propellant is crucial for achieving success in the design and development of rocket motors. This information must encompass all operating situations and design limits of the motor (Manash et al., 2019). Sutton et al. (2016) reported that the nature of the propellant determines the burning rate, and the combustion efficiency of composite propellants can be enhanced by modifying the propellant properties as follows:

- I. Incorporate a burning rate catalyst, sometimes referred to as a burning rate modifier, into the propellant mixture at a concentration of 0.1 to 3.0% by weight, or alternatively, increase the proportion of the current catalyst.
- II. Reduce the size of the oxidiser particles.
- III. Enhance the proportion of oxidiser.
- IV. Enhance the combustion heat of the binder and/or the plasticiser.
- V. Embed wires or metal staples into the propellant.

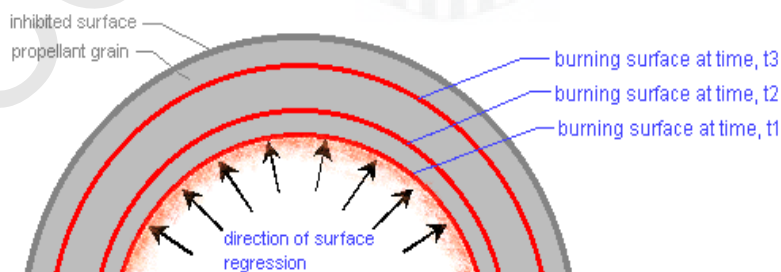


Figure 2.16: Burning surface regression of the composite solid propellant grain
(Source: Nakka, 1997)

The mechanisms occurring during propellant burning are complex. Therefore, precisely predicting a solid propellant's regression rate ($\dot{r}$) based on theoretical principles is challenging. Despite several academic attempts to forecast the pace at which propellant burns by modelling the underlying physical processes, their performance has been severely restricted. Instead, a practical correlation derived from empirical data has been established and is now employed to design and construct solid-propellant rocket engines. The pressure within the chamber influences the linear burning rate since the rates of gas phase reactions are crucial in supplying heat to the burning surface (Griego et al., 2019). The linear burning or regression rate ($\dot{r}$) may be determined using experimental methods, namely by utilising a strand burner, sometimes called a Crawford bomb. Crawford burner is the predominant technique for measuring the linear burning rate (Chandru et al., 2018). The schematic of a typical strand burner is presented in Figure 2.17. The apparatus comprises a high-pressure chamber, slender strands with a vertical propellant holder, a high-pressure N₂ gas cylinder and pipeline, an igniter, a surge tank, and other components. The propellant strand, which has a diameter of 5 mm or a dimension of 5 × 5 mm and a length of 100–250 mm, is affixed to a strand holder within a sealed bomb. The propellant strand must be restrained on the sides to burn one-dimensionally, like a cigarette (Yang et al., 2023).

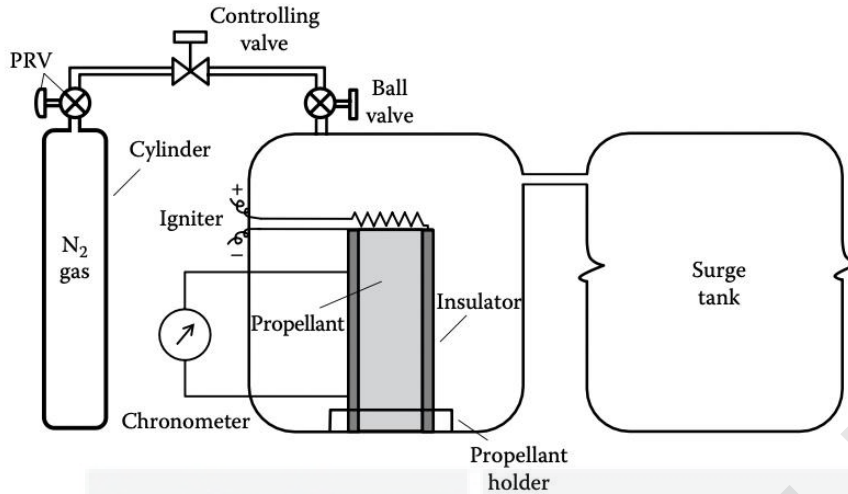


Figure 2.17: Crawford strand burner setup schematic diagram for burn rate testing

(Source: Mishra, 2017)

The pressure within the chamber highly influences the combustion rate of the propellant (Lang et al., 2006). The strand burner technique may readily determine the relationship between the chamber pressure (P_c) and the regression/burning rate ($\dot{r}$) of a certain propellant. The burning rate law may be established by running several tests at various pressure levels to find the empirical connection between the burning rate ($\dot{r}$) and the chamber pressure (P_c). The empirical burning rate law, known as Saint-Robert's law or Vieille's law, is extensively used and considered elegant (Kimura et al., 2016). It may be expressed as follows:

$$\dot{r} = aP^n \quad (15)$$

Where a is the empirical constant influenced by the initial temperature of the propellant grain P_c is the chamber pressure, n is known as the pressure exponent or combustion index, dependent on the constituent of the propellant.

The more general form of this empirical burning rate law is expressed as follows (Oluwoye et al., 2020):

$$\dot{r} = aP^n + b \quad (16)$$

where a and b are the empirical constants influenced by the initial temperature of the propellant grain for a particular propellant. For very high chamber pressure, particularly such as that prevailing in artillery, a linear burning law known as Muraour's law has been developed (Klinger et al., 2023):

$$\dot{r} = aPc + b \quad (17)$$

It should be noted that these correlations apply to both composite and double-base propellants. Nevertheless, these empirical burning rate equations are accurate within the specific limits of chamber pressure and beginning temperature of the propellant grain (Arkhipov et al., 2016). The remaining correlations for the burning rate are intended explicitly for scenarios in which the system is in a stable and unchanging state. Nevertheless, unpredictable combustion may manifest at chamber pressures that were not accounted for in the empirical regression rate equation (Pylypenko et al., 2020). It is necessary to use specified units when referring to these connections (Simontacchi et al., 2019). In addition, Vieille's Law is an empirical approximation that does not apply to all propellant regimes. Figure 2.18 shows plateau burning, a Vieille's Law deviation.

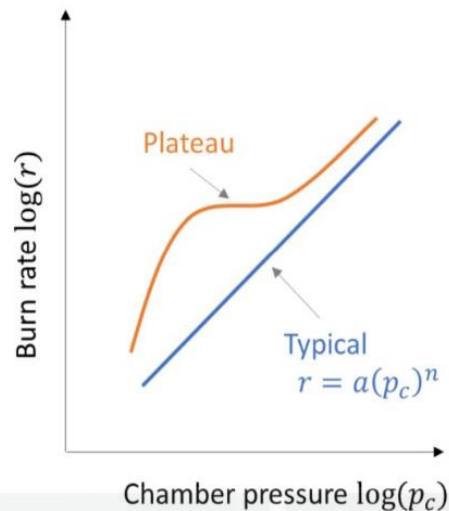


Figure 2.18: Vieille's Law may describe a typical propellant's burn rate and pressure dependency, which produces a straight line on a log-log diagram.

(Source: Vernacchia et al., 2017)

2.11 Burn Rate Behaviour Effect on The Performance of The Solid Rocket Motor

Burn rate properties are an essential parameter in the CSP study as these properties give a quantitatively and qualitatively precise prediction of the performance of the propellant before applying it to the rocket motor. Flame regression is the term used to describe the burning rate of solid propellant rocket motors, wherein the fuel grain ignites perpendicular to the burning surface. According to Szala et al. (2020), from the burn rate experiment lab works, some of the critical parameters for the rocket motor performance can be achieved theoretically, which are the thrust value, specific impulse, and characteristics velocity. In actual practical work, the rocket engineer will optimise and evaluate the rocket motor design to ensure the specifications fully fulfil the required missions (Cha et al., 2023). Besides, this will ensure that

the rocket motor will not undergo failure or, in the worst case, catastrophic failure.

The thrust value can be achieved from the burn rate testing, in which the rocket motor's performance can be predicted and optimised. Concerning Yang et al., 2023, the burn rate value influences the thrust of the rocket motor by varying the propellant mass flow rate. The burn rate determines how quickly the propellant is consumed. A higher burn rate means more propellant mass is burned per unit time (Sutton et al., 20218). The mass flow rate ($\dot{m}$) is given by:

$$\dot{m} = \rho \cdot A \cdot r \quad (18)$$

Where ρ is the propellant density, A is the burning surface area, and r is the burn rate. Theoretically, the higher the mass flow rate value of the CSP, the higher the thrust value generated by the rocket motor. The mass flow rate is a fundamental parameter in rocketry, as it directly influences the thrust produced by the engine through the relationship defined by the thrust equation:

$$F = \dot{m} \cdot v_e + (P_e - P_a) \cdot A_e \quad (19)$$

where $\dot{m}$ is the mass flow rate, v_e is the exhaust velocity, P_e is the exhaust pressure, P_a is the ambient pressure, and A_e is the area of the nozzle exit. Experimental works conducted by Yildiz et al. (2017) proved the relationship between the mass flow rate generated from the burn rate value and the thrust produced by the rocket motor in cold and hot gases. Figure 2.19 shows the relationship plot between the thrust and mass flow rate from the experimental data reported by (Yildiz et al., 2017).

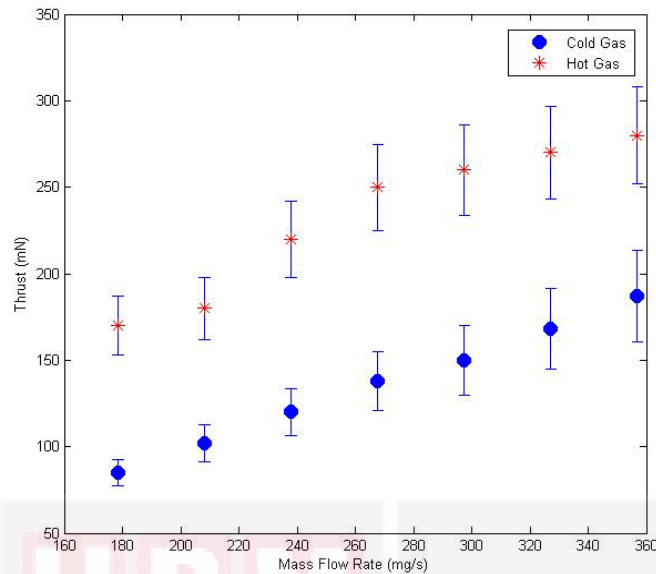


Figure 2.19: Effect of mass flow rate value on the thrust performance of the solid propellant rocket
(Source: Yildiz et al., 2017)

Furthermore, the burn rate value can be used to get the characteristic velocity of the rocket motor performance. For example, the higher the burn rate value, the higher the amount of exhaust gases, which more gas is produced per unit of time. This increases the mass flow rate, which combines with the exhaust velocity and results in higher thrust (Mutrakulcharoen et al., 2021). Moreover, Farhadi et al. (2020) claimed that a higher burn rate typically increases the pressure and temperature inside the combustion chamber. According to the thrust equation, this enhances the exhaust velocity, further contributing to greater thrust.

2.12 Combustion Mechanism Process of AP/HTPB-Based Composite Solid Propellant

CSP combustion comprises multiple phases and a complicated flame structure. The propellant is solid, yet key processes, such as fuel-oxidiser

combustion, occur in the gas phase (Gallier et al., 2016). Flames hang over the burning propellant. These flames heat the propellant surface, decomposing its solids into gases. Fuel vapour and oxidising species in gaseous breakdown products fuel flames. The combustion process has a crucial feedback loop. Fuel and oxidiser come from surface vaporisation from flame heat. This process's pace is determined by chemical kinetics, mass transport, and heat transfer in the combustion zone. According to the theory reviewed by Vernacchia et al. (2017), the combustion mechanism can be divided into 6 reactions. The illustration of the combustion mechanism of CSP can be shown in Figure 2.20.

- I. **Binder breakdown-** Heat flux from the flames heats the binder and decomposes it into a hydrocarbon gas at the binder surface. Solid metal particles are expelled from the dissolving binder if a metal fuel is present. This is an endothermic process.
- II. **AP condensed phase reactions-** At the surface of an AP particle, AP decomposes to give off gaseous, oxidising products. A liquid melt pool forms on the surface of the AP as an intermediate step. This reaction is exothermic.
- III. **AP flame-** Some AP products (NH_3 and HClO_4) burn near the AP particle surface in the gas phase. This is an exothermic process with a flame temperature of 1200 - 1400 K. The standoff distance between the AP flame and the propellant surface is determined by the velocity of the product gases and the reaction kinetics.

- IV. **The "primary" or "leading edge"**- The primary flame burns close over the boundary between an AP particle and the surrounding binder. At the boundary, oxidising vapours from the AP and hydrocarbon vapours from the binder are effectively premixed. This allows for a hot (~ 3000 K), intense flame close to the surface. The primary flame standoff distance is mainly set by kinetics.
- V. **The diffusion flame**- The diffusion flame is cooler and exists further from the surface. The oxidiser and fuel vapours, which were not consumed by the primary flame, diffuse toward each other, meeting at the stoichiometric surface of the diffusion flame. In fuel-rich propellants, it closes over the AP particle. As the name implies, the location and combustion rate of the diffusion flame are set by molecular diffusion.
- VI. **Metal droplet combustion**- Particles from solid metal fuel are ejected from the decomposing binder surface and are warmed by passage through the flames. During this time, the particles agglomerate, melt into droplets, begin to boil and ignite. Combustion occurs on a comet-shaped around the droplet. The metal droplets burn far from the propellant surface, roughly 2~200 mm (compared to the ~ 500 μm height of the flame structure). By the time the metal burns, most of the usual oxidising species have been consumed by the primary and diffusion flames. Instead, the metal is oxidised by reducing H_2O and CO_2 in the exhaust to H_2 and CO .

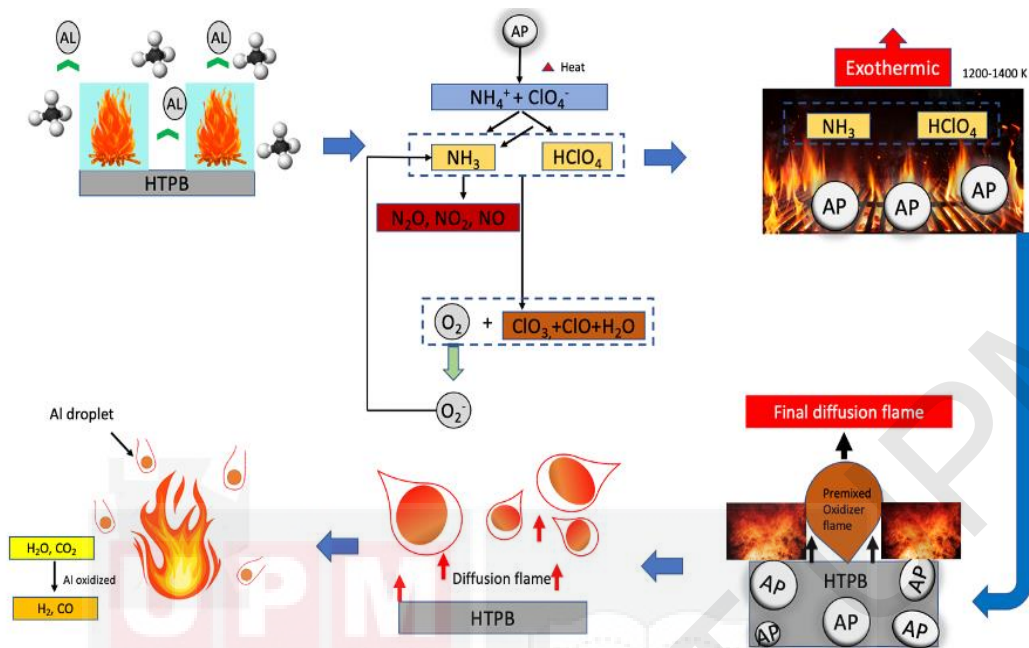


Figure 2.20: Overview of combustion mechanism process in AP/HTPB composite solid propellant

By understanding the combustion mechanism in AP-based CSP, the specific specification of the rocket propellant can be optimised in the development of the CSP. Besides, in studying the combustion of the AP-based CSP, some parameters from the experimental works can be used to achieve the rocket motor's performance, which is thrust and specific impulse. The most significant combustion test used by many rocket scientists in Duan et al. (2022) to determine rocket motor performance is bomb calorimetry testing. Bomb calorimetry is a fundamental test in solid propellant studies that provides critical information on the propellant's energy content, performance, combustion efficiency, and safety (Dong et al., 2022). This data is essential for optimising propellant formulations, ensuring quality and reliability, and meeting regulatory requirements. The bomb calorimeter measures the heat of combustion of the propellant, which can determine the energy content of the

propellant and directly influences the rocket motor's performance. Higher energy content typically translates to higher thrust and better efficiency. Besides, An et al. (2022) reported that bomb calorimetry provides insights into the combustion efficiency of the propellant. Complete combustion releases the maximum amount of energy, while incomplete combustion indicates potential issues with the formulation or combustion process.

Theoretically, CSP needs high energy content to produce a high thrust value to fill the specific flight mission (Unger et al., 2020). The thrust produced by a rocket is directly proportional to the energy released during the combustion of the propellant. A higher heat of combustion means more energy is released, leading to greater thrust and better overall performance of the rocket. This is because a higher heat of combustion means more energy is available to convert into kinetic energy of the exhaust gases (Kuzmin et al., 2015). This increased energy translates directly into higher thrust. Moreover, when a propellant with a high heat of combustion burns, it generates more heat, increasing the temperature, pressure, and exhaust velocity during combustion. Higher pressure in the combustion chamber leads to a greater force exerted on the rocket's nozzle, resulting in increased thrust. The relationship between chamber pressure, temperature, and exhaust velocity to the thrust can be seen in the previous simplified thrust equation (19). The effective exhaust velocity is influenced by the energy released during combustion as higher heat of combustion results in higher temperatures, which increases the velocity of the exhaust gases as they are expelled through the nozzle. Thus, this high exhaust velocity value will result in a high specific impulse of the rocket motor,

producing more thrust per unit propellant mass. This relationship can be seen by the specific impulse equation:

$$Isp = \frac{V_e}{g_o} \quad (20)$$

Where Isp is a specific impulse, V_e is effective exhaust velocity and g_o is the standard acceleration due to gravity.

Additionally, Sinditskii et al. (2015) claimed that rocket propellants require a high amount of energy due to the energy density of the propellant contained in the rocket motor. A high heat of combustion indicates a high energy density, meaning that more energy is packed into a smaller propellant volume. This is crucial for limited space and weight applications, such as missiles, space launch vehicles, and military rockets (Tola et al., 2018).

2.13 Statistical Design of Experimental Methodology

The analysis of mechanical properties and combustion characteristics, specifically burn rate, are determined by many manipulated variables to ensure the analysis is reliable and realistic. For example, in burn rate testing, the propellant strand sample with different formulations must be burned at different pressures because, in actual rocket motor applications, the pressure in the rocket motor chamber is different when the combustion process takes place. Besides, during the burning of the rocket propellant grain inside the rocket motor chamber, the temperature also varies due to the increasing pressures (Collard et al., 2019). Thus, these parameters will influence the tensile strength of the propellant grain. In this research study, the mentioned testing will consider all the parameters that influence all the output values, and

these procedures are also followed by the standard testing methodology that other researchers have finalised. Due to the number of parameters in each of the experimental works, the design of experiments must be done to achieve the maximum information and outputs from the experiment. Besides, Antony et al. (2023) stated that designing the experiment can save cost and time, and it helps to identify the most significant factors or manipulated parameters that affect most of the output value.

2.13.1 Response Surface Methodology (RSM) in Design of Experiment (DOE) Approach

Experiments can be developed using Factorial design, Taguchi robust design, or Response Surface Methodology (RSM) based on process parameters and levels. The goal is to reduce the number of trials and create a mathematical model for predicting a response. Analysis of variance can be used to determine which factors have a substantial influence on the answer. Several researchers, including Behera et al. (2018), have utilised the Taguchi approach to construct experiments and improve process parameters for a specific target function. Response surface methodology (RSM) is a mathematical and statistical approach for constructing experiments. The goal is to optimise a response impacted by several independent factors (Khuri et al., 2018). Furthermore, it is beneficial when the objective is to optimise a response (output) variable impacted by several independent factors. RSM helps to investigate the link between input factors and response by fitting a mathematical model to experimental data (Mahjub et al., 2020). The method entails running a series of tests at various factor levels to model the response

surface and then analysing the results to select the best input variables. Researchers have utilised response surface methods to optimise process parameters and create a regression equation to predict outcomes.

Researchers (Tola et al., 2018) employed the RSM approach to improve process parameters, including casting, and created regression equations to predict output response. Besides, experimental research conducted by (Roslan et al., 2024) utilised RSM to prepare nitrocellulose propellant formulation from nata de coco. The study suggests that the response surface approach is a promising strategy for optimising process parameters for a specific goal function. Developing a mathematical model can improve response prediction accuracy (Pandey et al., 2021). Using the RSM in the study of solid rocket propellants can be beneficial for optimising various factors that influence the performance of the propellant. For example, RSM can help optimise the composition of these ingredients to achieve desired performance characteristics like thrust, burn rate, and specific impulse and RSM can be applied to optimise processing conditions, such as mixing time, curing temperature, and pressure, to ensure uniformity and enhance propellant performance (Adeniyi et al., 2021). All these advantages and uses of RSM can significantly help minimise costs and time since this study about the solid propellant is a bit expensive, especially regarding raw materials.

2.13.2 Factorial Design (FD) Approach

Factorial design (FD) is prevalent in several scientific inquiries and industrial uses to identify significant components, owing to its cost-effectiveness and

adaptability (Gill et al., 2021). This strategy is extensively documented in the literature. Adams et al. (2020) suggest that estimating lower-order effects is especially useful for screening studies with a more significant number of components and a smaller number of runs. This study only considers the primary effects and two-factor interactions while excluding higher-order effects, which involve the interaction of three or more components. According to Kleijnen et al. (2018), the three basic concepts of effect hierarchy, effect sparsity, and effect heredity serve as the foundation for the FD analysis. These concepts are crucial for narrowing down the potential models (after the specified primary effects and interactions) and determining the optimal model. The idea of effect hierarchy asserts that primary effects often explain the most significant amount of variance in the response. According to Kadaganchi et al. (2015), second-order effects, such as interaction effects and quadratic terms, have more significance than third-order and higher effects. FD is composed of two levels, specifically high (+) and low (-), for each component that was examined (Keshtegar et al., 2018). Nevertheless, the number of levels per element may be expanded to three by including centre points in each block. This design employs a carefully selected subset of treatment combinations necessary for conducting the whole factorial experiment (Said et al., 2015). FD only allows for 2 or 3 levels per factor (also with a maximum of 15 factors). However, FD can still provide adequate information, such as the number of significant factors, the interaction between factors, and the optimum point, for further experimentation (Keharom et al., 2016).

2.14 Summary

Composite solid propellant (CSP) is a type of rocket fuel mainly consisting of oxidiser, fuel, and polymer binder. Currently, AP is the oxidiser type most commonly used in CSP applications because of its tremendous performance properties. However, a recent issue has highlighted the effect of using this type of oxidiser on the environmental aspect in which it emits a lot of HCl gases as combustion products. Although some researchers have put an effort into reducing the HCl gas, most of the work is not practical with the application. This is because the research done by other researchers is just up until the thermal decomposition of AP and burn rate studies. There is still insufficient data on mechanical and HCl concentration to align with allowable ppm HCl value. Besides, these mechanical properties in solid propellant study are very important as this data gives more information about the safety, reliability of the applications, and structure integrity of the CSP.

At present, efforts to reduce HCl gases in AP-based CSP are being made by incorporating metal additives, a combination of dual oxidisers, and entirely replacing AP with another oxidiser. Incorporating metal additives can give a higher burn rate performance and reduce HCl as a combustion product by scavenging the HCl. However, there is no data on the mechanical properties of this work, and it is not practically reliable as the cost and the complexity of fabrication are very high. It is thus necessary to strategise ways to reduce HCl gases, which may reduce the environmental problem and cost-effective rocket fuel. Table 2.14 illustrates the critical analysis of the literature findings on the recent efforts to mitigate HCl as a combustion by-product of CSP.

Table 2.14: Critical analysis on mitigating HCl gases efforts as combustion by-products of CSP

Sample	LTD & HTD (°C)	Tensile strength (MPa) at 20°C	Chlorine concentration (ppm)	Burn rate at 3 atm (mm/s)	Reference
AP/ADN/HTPB CSP	N/A	2.64	N/A	7.55	Sims et al., 2022
AP/HTPB CSP	200 & 387	2.54	692.5	5.42	Mason et al., 2019
HNF/HTPB CSP	197 & 301	N/A	N/A	7.92	Wang et al., 2022
RDX/HTPB CSP	N/A	3.1	N/A	7.81	Khichar et al., 2019
AN/HTPB CSP	300 & 331	1.97	321.4	4.79	Kumar et al., 2018
AP/HTPB/Li CSP	205 & 342	2.47	362.1	5.32	Lawrence et al., 2019
AP/HTPB/Mg CSP	261 & 372	N/A	361.1	6.01	Vellaisamy et al., 2020
AP/HTPB/Li-Mg CSP	251 & 366	2.73	351.9	6.22	Terry et al., 2016

N/A: Not applicable

CHAPTER 3

METHODOLOGY

3.1 Overview

This chapter discussed the research flowchart, materials used, experimental design setup, and testing procedure in this research work. Additionally, the sample preparations of KMnO_4/AP and KMnO_4/AP in composite solid propellant systems were examined in detail. Standard procedures for each experiment and microstructural and element characteristics tests were presented. Figure 3.1 illustrates the flowchart for this study.

3.2 General Method of Approach

Generally, this study aims to fabricate KMnO_4/AP dual oxidiser in AP/HTPB-based composite solid propellant systems and evaluate HCl concentration as a combustion product and combustion performance. Therefore, all the processes required a lot of procedures and safety precautions as this research deals with explosive materials. Besides, the method in each procedure required precise quantitative and qualitative parameters to ensure the samples produced followed the theoretical. The flow chart describing the steps taken during this research study is shown in Figure 3.1, which also illustrates the outline plan of the investigation. This work is divided into two main experimental parts: the characterisation and testing KMnO_4/AP and composite solid propellant (CSP) with KMnO_4/AP as a dual oxidiser.

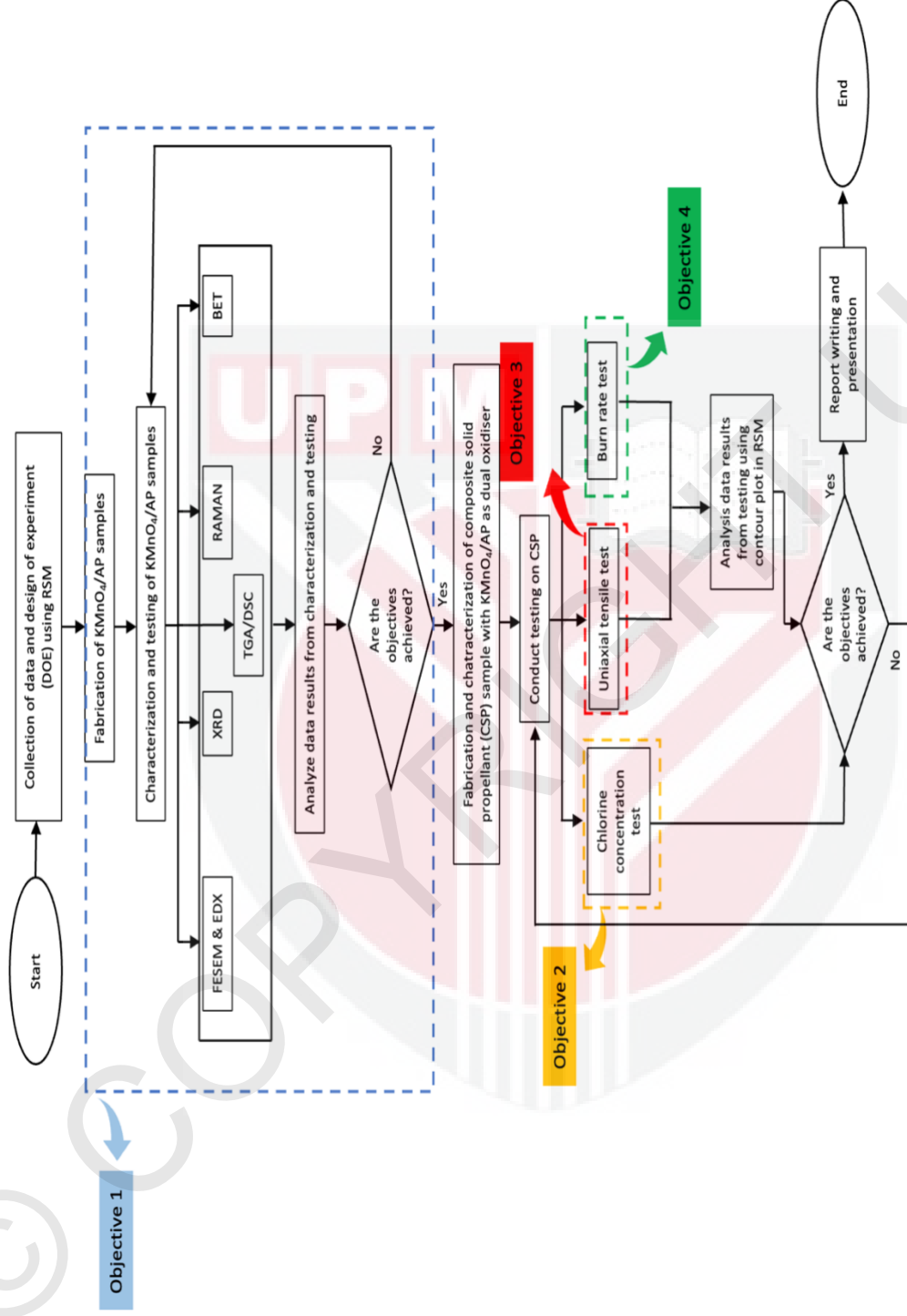


Figure 3.1: Flow chart of overall research study

3.3 Materials Sample Preparation for Experimental Works

3.3.1 KMnO_4 /AP Synthesis Process and Sample Size

KMnO_4 crystals were ground and blended with AP powder for 30 minutes using agate mortar, incorporating 1mL of ethanol for another 30 minutes to produce a 20:80 ratio with a total weight of 3g KMnO_4 /AP as in Chen et al. (2018), where the author synthesised manganese oxide (MnO_4) with AP. This is to ensure the uniform dispersion of the samples. The suspension was filtered to collect a mixture of KMnO_4 /AP using vacuum filtration. Next, KMnO_4 /AP was dried at 70°C for one hour and prepared for characterisation. The samples were stored in a desiccator filled with silica gel to prevent the absorption of moisture that would affect the material's properties (Fu et al., 2008). Figure 3.2 illustrates the synthesis method flow chart for KMnO_4 /AP, while Figure 3.3 shows the visualisation of the KMnO_4 /AP synthesis process. Samples of KMnO_4 /AP were prepared in weight ratios of 20:80, 40:60, 60:40, and 80:20, together with pure AP and pure KMnO_4 for characterisation and comparison analysis, as presented in Table 3.1.

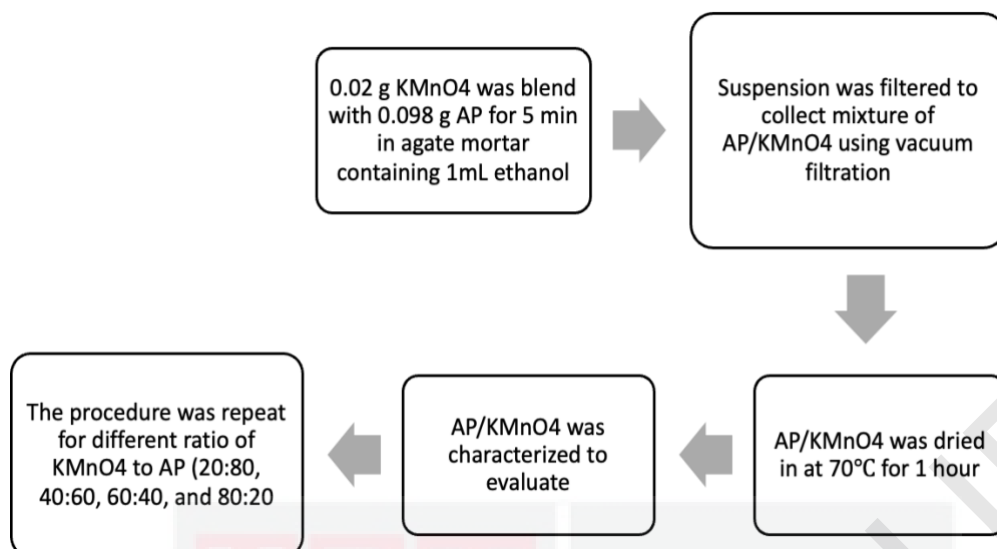


Figure 3.2: Flow chart of KMnO₄/AP synthesis process

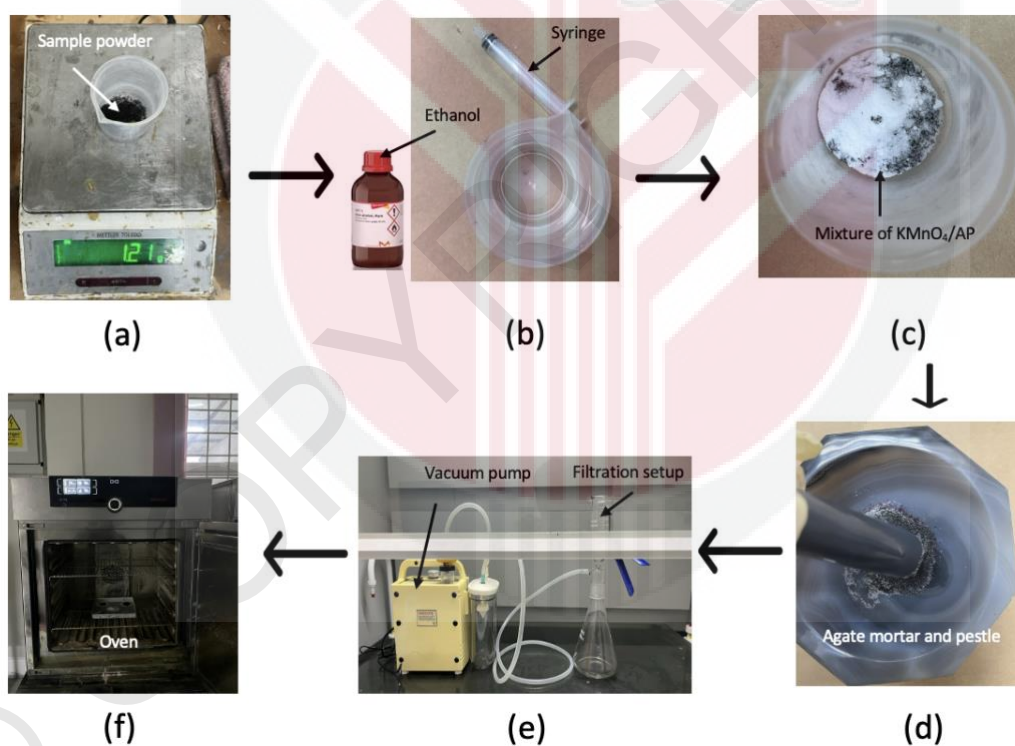


Figure 3.3: Synthesis process of KMnO₄/AP using agate mortar pestle (a) Weigh (b) Mix with ethanol (c) Mix KMnO₄ with AP (d) Mix and crush using agate mortar and pestle (e) Vacuum filtration and (f) Drying

Table 3.1: Sample size and the chemical composition of KMnO_4/AP dual oxidiser

Label	AP	KMnO_4	KMnO_4/AP (20:80)	KMnO_4/AP (40:60)	KMnO_4/AP (60:40)	KMnO_4/AP (80:20)
KMnO_4 to AP ratio	-	-	20:80	40:60	60:40	80:20
AP	350 g	-	280 g	210 g	140 g	70 g
KMnO_4	-	350 g	70 g	140 g	240 g	280 g
Total weight	350 g	350 g	350 g	350 g	350 g	350 g

3.3.2 AP-Based Composite Solid Propellant Sample Fabrication Process

Figure 3.4 illustrates a flowchart depicting the combination and production process of CSP. Besides the sample preparation steps are shown in the flow chart in Figure 3.5. Before starting the process of CSP mixing, all the chemicals and powder were weighed and sieved, as illustrated in Figures 3.6 (a) and 3.6 (b), respectively, according to the formulation in Table 3.2. Firstly, dioctyl adipate (DOA) plasticiser was added to the polymer binder HTPB, and the mixture was stirred for 5 minutes to be pre-mixed. Secondly, aluminium (Al) powder was added batch by batch into the pre-mix in the kneading mixer at a temperature of 45 °C, as shown in Figure 3.6 (c). The mixer was run for 5 minutes for each batch. Next, the first increment of KMnO_4/AP as an oxidiser was added to the mixture and allowed to react for 5 minutes. Then, the second and third increments of KMnO_4/AP were added and allowed to react for 25 minutes, respectively. Given that the oxidiser is the primary composition in the CSP formulation, it must be divided into three increments when added into the mixture to ensure the homogeneity of the mixture is in good condition. Next,

toluene diisocyanate (TDI) as a curing agent was added drop by drop while mixing and ran for 40 minutes. After that, the propellant slurry was cast into the sample mould, as in Figure 3.6 (d) and cured in a 60 °C oven for 5 days, as shown in Figure 3.6 (e). The cured samples in Figure 3.6 (f) were ready to be tested and evaluated for their performances.

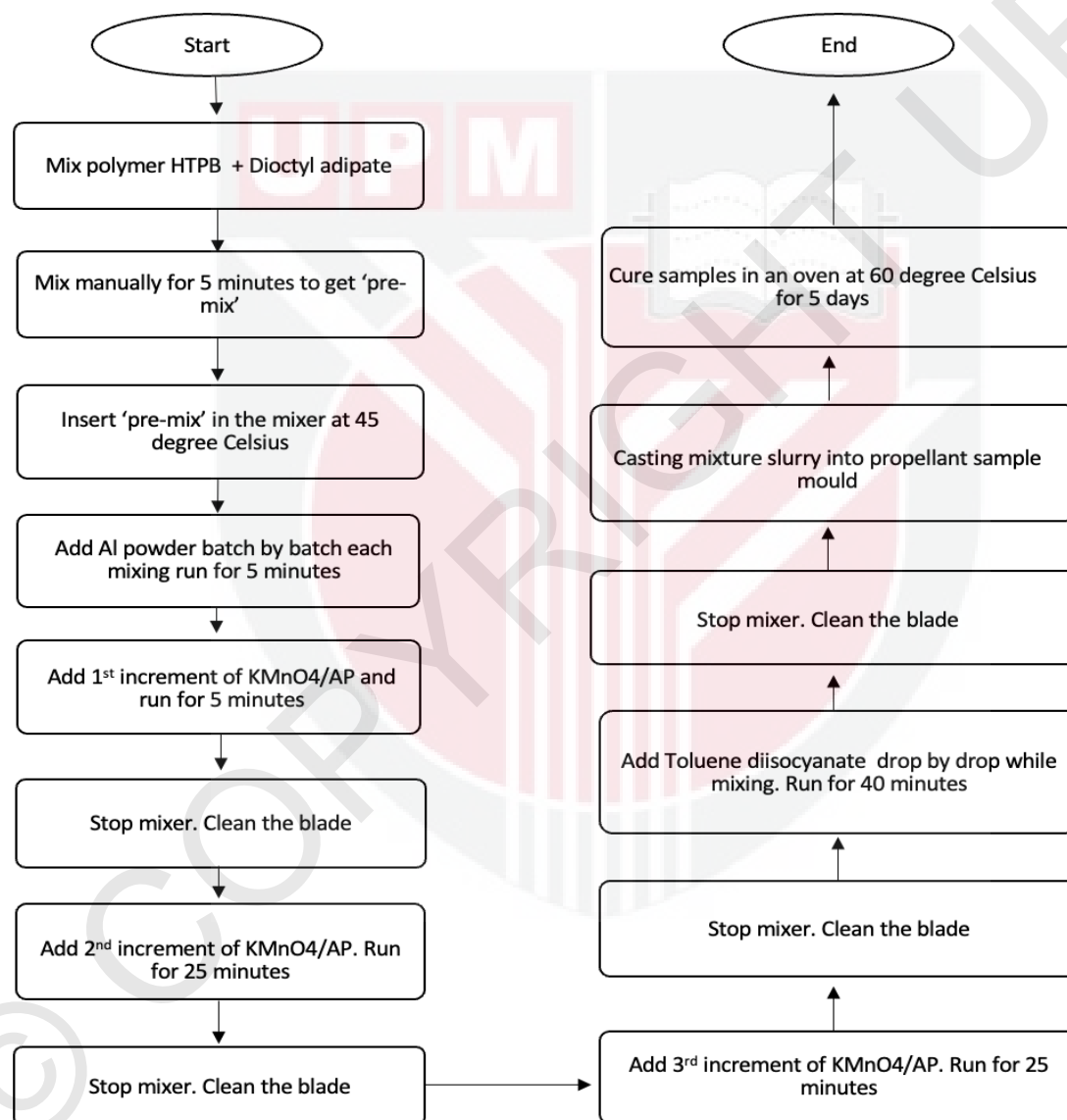


Figure 3.4: Flow chart of composite solid propellant sample fabrication process

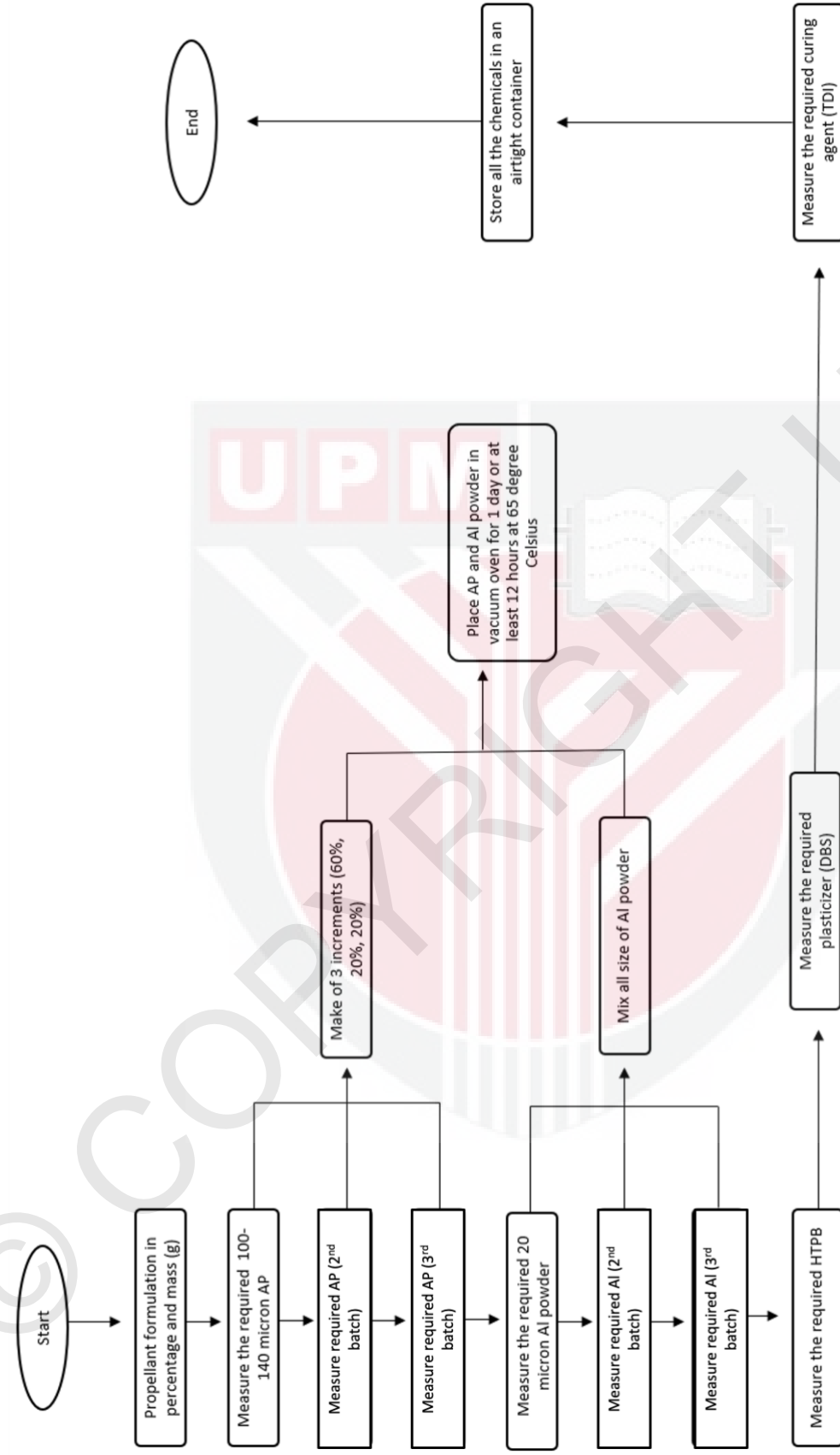


Figure 3.5: Materials and chemicals preparation in composite solid propellant fabrication process flow chart

Table 3.2: Composition and formulation of composite solid propellant (CSP) samples (a) AP-based CSP, (b) KMnO_4/AP (20:80) based CSP, (c) KMnO_4/AP (40:60) based CSP, (d) KMnO_4/AP (60:40) based CSP, and (e) KMnO_4/AP (80:20) based CSP

Materials		Size	Composition (%)	Weight (g)
Oxidiser	AP	140 μm	70	350
	KMnO_4	150 μm	-	-
Fuel	Al	20 μm	4	20
		16 μm	4	20
		13 μm	4	20
Binder	HTPB	-	13.5	67.5
Curing Agent	TDI	-	1	5
Plasticiser	DOA	-	3.5	17.5
Total			100.00	500

(a)

Materials		Size	Composition (%)	Weight (g)
Oxidiser	AP	140 μm	56	280
	KMnO_4	150 μm	14	70
Fuel	Al	20 μm	4	20
		16 μm	4	20
		13 μm	4	20
Binder	HTPB	-	13.5	67.5
Curing Agent	TDI	-	1	5
Plasticiser	DOA	-	3.5	17.5
Total			100.00	500

(b)

Materials		Size	Composition (%)	Weight (g)
Oxidiser	AP	140 μm	42	210
	KMnO ₄	150 μm	28	140
Fuel	Al	20 μm	4	20
		16 μm	4	20
		13 μm	4	20
Binder	HTPB	-	13.5	67.5
Curing Agent	TDI	-	1	5
Plasticiser	DOA	-	3.5	17.5
Total			100.00	500

(c)

Materials		Size	Composition (%)	Weight (g)
Oxidiser	AP	140 μm	28	140
	KMnO ₄	150 μm	42	210
Fuel	Al	20 μm	4	20
		16 μm	4	20
		13 μm	4	20
Binder	HTPB	-	13.5	67.5
Curing Agent	TDI	-	1	5
Plasticiser	DOA	-	3.5	17.5
Total			100.00	500

(d)

Materials		Size	Composition (%)	Weight (g)
Oxidiser	AP	140 μm	14	70
	KMnO ₄	150 μm	56	280
Fuel	Al	20 μm	4	20
		16 μm	4	20
		13 μm	4	20
Binder	HTPB	-	13.5	67.5
Curing Agent	TDI	-	1	5
Plasticiser	DOA	-	3.5	17.5
Total			100.00	500

(e)

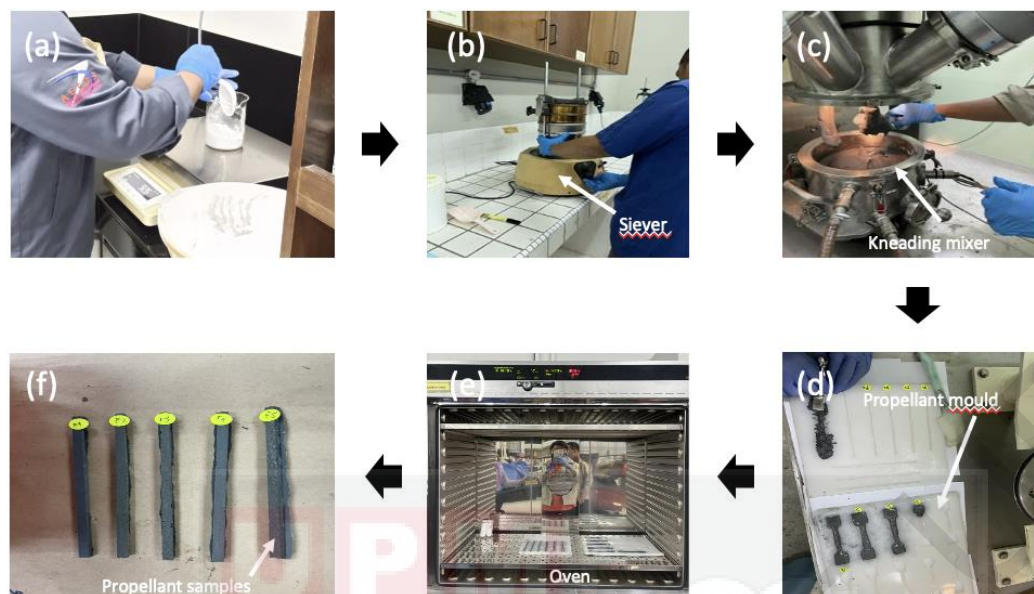


Figure 3.6: Fabrication process of composite solid propellant (a) weighing, (b) sieving, (c) mixing, (d) casting, (e) curing, and (f) cured samples

The weight of KMnO_4 and AP were calculated based on the weight ratio of KMnO_4 to AP. For example, to obtain 20% of KMnO_4 in the whole percentage of oxidiser, 14% of KMnO_4 , which consists of 70g from the whole weight of the oxidiser, is needed for formulation (20:80). The calculation of the weight per cent required for KMnO_4 to AP is the same for all the formulations. Besides, all the weight percentages of other chemicals, including Al, plasticiser, curing agent, and binder, are constant for all the formulations.

3.4 Characterization of KMnO_4 /AP Dual Oxidiser and Composite Solid Propellant (CSP) Samples

3.4.1 Morphological Analysis

Scanning Electron Microscopy (SEM) was used to analyse external morphology, such as the structure, crystalline structure, and orientation of the

samples' materials. SEM imaging was conducted using an FEI Model NOVA NANOSEM 230 for chemical and structural characterisation of specimens with an acceleration voltage of 120 kV. Microstructural analysis was performed on KMnO_4/AP dual oxidiser and CSP samples. Sample specimens were prepared by attaching them on aluminium sample stubs with carbon conductive tape. They were then sputter coated with gold-palladium using Baltec SCD-005 Sputter Coater to produce the best quality and high-resolution image. The stub with coated specimens was inserted into the SEM sample chamber for observation. The elemental analysis in the samples was also conducted using Energy Dispersive X-ray (EDX) analysis using Oxford Instruments (Max 20).

3.4.2 Thermal Analysis

Thermal study is essential for comprehending composite solid propellants' behaviour, stability, and performance. These propellants, formulated using ammonium perchlorate (AP) and hydroxyl-terminated polybutadiene (HTPB), consist of various components that experience thermal degradation, oxidation, and combustion at distinct temperatures. Thermal analysis techniques offer insights into these processes, guaranteeing the propellant's stability during storage, predictability during operation, and safety while handling. Thermogravimetric Analysis (TGA) is an essential thermal analysis method for examining composite solid propellant (CSP) formulated using AP and HTPB. TGA is a method for measuring the weight loss of a material due to either an increase in temperature or time and essential information regarding the thermal stability, breakdown, and characteristics of propellants.

Differential Scanning Calorimetry (DSC) quantifies the heat flow transfer into or out of a sample during heating, cooling, or isothermal maintenance. This approach elucidates the characteristics of endothermic (heat-absorbing) and exothermic (heat-releasing) reactions in solid propellants. Additionally, DSC is a technique to measure temperature and physical property changes in samples over time. DSC can also detect the exothermic responses associated with the decomposition of AP and other oxidisers and phase transitions in the HTPB, such as glass transition, melting, or crystallisation.

In this study, the catalytic effects of KMnO_4 on the thermal decomposition of AP were studied and analysed by DSC and TGA using Mettler Toledo (Model TGA-DSC HT 3). The samples were held at $25\text{ }^\circ\text{C}$ for 1 min before heating up to $1000\text{ }^\circ\text{C}$ with a heating rate of 20K/min . A nitrogen gas flow rate of 50 mL/min was applied. All the sample results were plotted in one graph of TGA and DSC to compare with the pure AP decomposition. The thermal decomposition analyses were measured for both types of samples, KMnO_4/AP dual oxidiser and KMnO_4/AP -based CSP. The purpose is to observe the effect of KMnO_4 on thermal decomposition behaviour in AP-based CSP systems. Specimens, in powder and solid, weighing approximately 20 mg , were placed in crucibles.

3.4.3 Crystallinity Structure Properties

X-ray diffraction (XRD) patterns were recorded from 30° to 90° with a diffractometer (Rigaku model: SmartLab 2, MiniFlex 600) using $\text{Cu K}\alpha$ ($\lambda = 1.542\text{ \AA}$) with an accelerating voltage of 40 KV . Data was recorded with a

counting rate of 4 %/min. The K α doublets were well resolved. The mean grain size was estimated from the integral widths of the X-ray peaks after numerically removing the machine error and correcting it for instrumental broadening. Origin student version 2024; Software for Data Analysis and Graphing; OriginLab: software was utilised to analyse peak broadening and calculating the crystallinity of the powder by the Debye-Scherrer formula given by equation (21) and (22) (Singh et al., 2019). The full-width at half-maximum (FWHM) of each peak was obtained using the software, and the D-spacing was calculated by Bragg's law, as shown in equation (21) as follows:

$$n\lambda = 2d\sin\theta \quad (21)$$

Where n represents the order of reflection, λ is the wavelength of the X-ray from the Cu source equating to 0.1542 nm, where d indicates the D-spacing or lattice spacing, and θ is the peak position acquired from the XRD profiles.

Additionally, the Scherrer equation was used to determine the crystallite dimensions, such as the crystallite diameter (D), as shown in equation (22):

$$D = (K\lambda)/(\beta \times \cos\theta) \quad (22)$$

Where K is the Scherrer constant corresponding to 0.94 or 1.84, depending on the calculations of the crystallite diameter or crystallite height, respectively. Here, β refers to the full width at half-maximum (FWHM) of the aluminium peaks, which can be calculated from the XRD profiles; λ and θ represent the wavelengths of X-ray from Cu source and peak position, respectively, as described in Equation (21) (Rijesh et al., 2018). Besides, the X'Pert HighScore software was utilised to determine specific crystallographic planes in a crystal

lattice and analyse the peaks to elucidate the material's structure, composition, and properties.

3.4.4 Surface Area Analysis

The specific surface area is an important parameter in this study to understand the performance and characteristics of KMnO_4/AP as a dual oxidiser, especially in applications such as catalysis, adsorption, and gas-solid interactions. BET analysis, or Brunauer-Emmett-Teller analysis, is a technique used to measure the specific surface area of a material, particularly porous substances such as powders and catalysts. Besides, BET analysis is employed to determine this surface area by studying the adsorption of gas molecules onto the surface of the materials. In this study, the BET surface area analysis of synthesised samples was determined using an instrument called the Micromeritics model Tristar II Plus.

The basic principle of BET analysis involves measuring the amount of gas adsorbed at different relative pressures. Nitrogen gas is used as the adsorbate because it is inert and widely available. The adsorption data is then analysed using the BET equation, which relates the amount of adsorbed gas to the surface coverage and provides information about the monolayer adsorption.

The BET equation used is as follows:

$$\frac{P}{V_o - V} = \frac{1}{C} + \frac{C-1}{C} \frac{P_o}{V_m} \quad (23)$$

Where P is the equilibrium pressure of the gas, V is the volume of gas adsorbed, V_o is the volume of the gas at standard temperature and pressure

(STP), P_o is the saturation pressure of the adsorbate at the temperature of the experiment, C is a constant related to the energy of multilayer adsorption, and V_m is the monolayer volume of gas adsorbed.

3.4.5 Molecular Interaction Analysis

Raman spectroscopy is a powerful analytical technique used in materials science to study molecular composition, chemical structure, and molecular interactions within a material. In this study, RAMAN analysis was conducted to achieve valuable information about the chemical bonding in KMnO_4/AP dual oxidiser. Raman spectra of the samples were recorded in the frequency range of $200\text{--}2000\text{ cm}^{-1}$ using a Raman spectrometer (WITec Alpha 300R) with a laser excitation wavelength of 532.167 nm . When the incident light interacts with a material, some of it is scattered at the same wavelength (Rayleigh scattering), while a small fraction undergoes inelastic scattering. The inelastically scattered light is shifted in frequency due to the vibrational and rotational modes of the material, and this shift is known as the Raman shift.

3.4.6 Heat of Combustion Analysis

The efficiency of the KMnO_4 in AP-based CSP in converting its chemical energy into thermal energy during combustion was investigated through the heat of combustion analysis. The heat of combustion is a key parameter for evaluating the energy output of the propellant and is directly related to the rocket motor's specific impulse (I_{sp}). Moreover, the heat of combustion testing helps in quantifying the impact of KMnO_4 on the energy release of the propellant. It can reveal whether this KMnO_4 improves combustion efficiency,

burn rate, and energy output. This study obtained calorimetric values using a bomb calorimeter (Parr 6100 instruments, Germany). The schematic diagram of the bomb calorimetry setup is shown in Figure 3.7 (a).

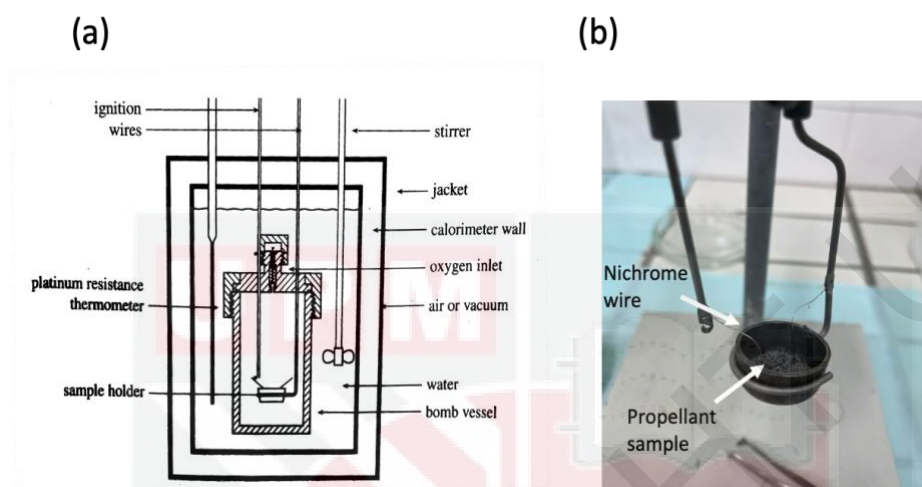


Figure 3.7: Bomb calorimetry (a) schematic diagram setup (b) propellant setup in a crucible of bomb calorimetry

The densities of propellant compositions were determined by a Mettler density kit (density 1.432 g cm³, heat of formation 565.8 kJ mol). The samples of CSP were measured and attached to ferrum wire before being loaded into a bomb calorimetric chamber. Then, the propellant sample was touched to the nichrome wire connected to the fuse for ignition, as in Figure 3.7 (b). A water bath jacket was used to surround the bomb to minimise heat exchange with the surroundings and to absorb the heat released during the reaction. The observed heat of combustion values were tabulated. Besides, the combustion efficiency of each of the samples was calculated using the following equation using the theoretical value:

$$\text{Combustion efficiency (\%)} = \frac{\text{Heat output}}{\text{Heat input}} \times 100 \quad (24)$$

Where heat output is the actual heat released during combustion, and heat input is the theoretical maximum heat that could be released during combustion based on the heat of combustion data. Heat input is taken from (Rao et al., 2016) as 1251 cal/g. The heat of combustion value can be determined using follows equation, and all the parameters in the formula are calculated and can be integrated straight away from the machine:

$$Q = \frac{C\Delta T - q_1}{m} \quad (25)$$

where Q is the heat of combustion (J/g); C is the thermal capacity of the calorimeter (J/K); ΔT is the measured temperature increase during combustion ($^{\circ}\text{C}$); q_1 is the heat of the explosion of the initiation wire (J); m is the mass of the sample (g).

3.5 Experimental Testing and Analysis Procedure

3.5.1 Hydrochloric Acid (HCl) Gases Concentration in Combustion By-Product of Composite Solid Propellant (CSP) Samples Test

The concentration of hydrochloric acid gases (HCl) as a combustion by-product of each combusted sample is measured using a gas-bubbling apparatus, followed by Mohr's titration method. The concentration of the dissolved HCl from the bubbling gas setup employed in the current investigation was analysed using Mohr's technique. Doll et al. (1992) utilised the gas bubbling method, employing a wet bomb, to evaluate the dissolved HCl content of water resulting from the burning of Mg metalised propellant. After that, many researchers used this method to evaluate the HCl concentration by-product from rocket propellant. For example, Vellaisamy et

al. (2020) investigated the effect of metal additives on HCl concentration as a combustion by-product of AP-based CSP. Furthermore, Mohr's method is a widely used analytical technique for determining the concentration of chloride ions in a solution. This method follows the standard of water quality determination of chloride (ISO 9297:1989). Figure 3.8 (a) reveals the schematic diagram for trapping the exhaust gases from the combustion of propellant samples using gas bubbling methods, and Figure 3.8 (b) illustrates Mohr's titration method.

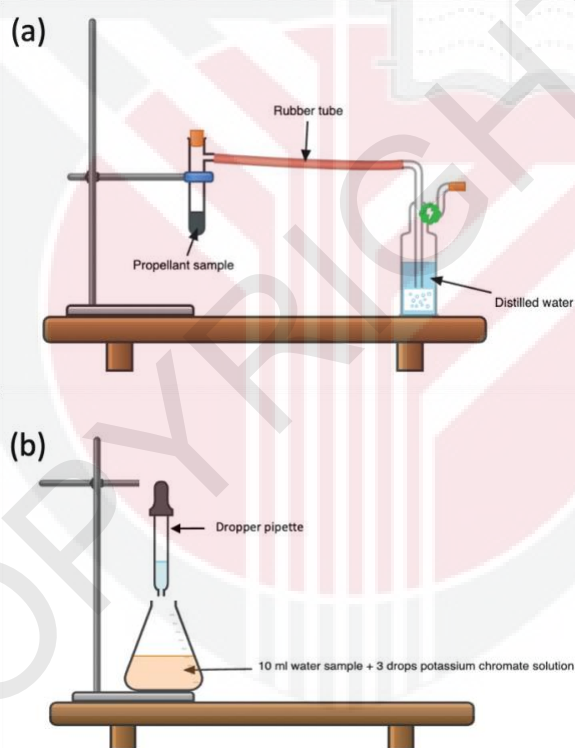


Figure 3.8: Schematic diagram of (a) gas bubbling setup and (b) Mohr's method on titration of HCl gases

This experiment aimed to investigate the impact of KMnO_4/AP as a dual oxidiser with different ratios on the decrease of harmful hydrogen chloride (HCl) emissions from AP-based CSP. A sample CSP of 6mm x 6mm x 100mm

was cut as in experimental work by Vellaisamy et al. (2020), and a 5 cm visco fuse wire was attached to the propellant sample, as shown in Figure 3.9 (a). Then, the CSP sample was put in the test tube with a side arm and a stopper at the top. The visco fuse wire was ignited using fire when the setup was ready to ignite the sample. Figure 3.9 (b) shows the CSP samples used in this experimental work.

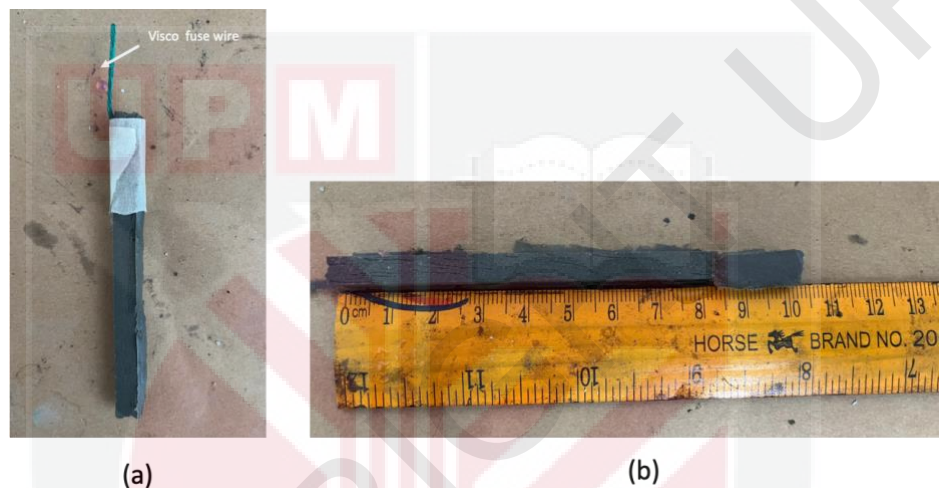


Figure 3.9: (a) CSP sample with visco fuse wire (b) 6mm x 6mm x 100mm propellant sample

The rubber tube connection is established by attaching the side arm test tube to the nozzle of a 2L wash bottle. A wash bottle containing 0.8L of distilled water was utilised to pass the exhaust gases through the water by means of bubbling. A glass tube with a diameter of approximately 0.3 meters is submerged in distilled water to allow the exhaust gas to create bubbles. The tests to collect exhaust gas were conducted under an inert environment and ambient pressure. Following the release of exhaust gases, the water sample is subjected to titration to determine the chloride concentration of the exhaust

gases. Figure 3.10 (a) illustrates the gas bubbling setup used in this research work, and Figure 3.10 (b) shows Mohr's titration setup.

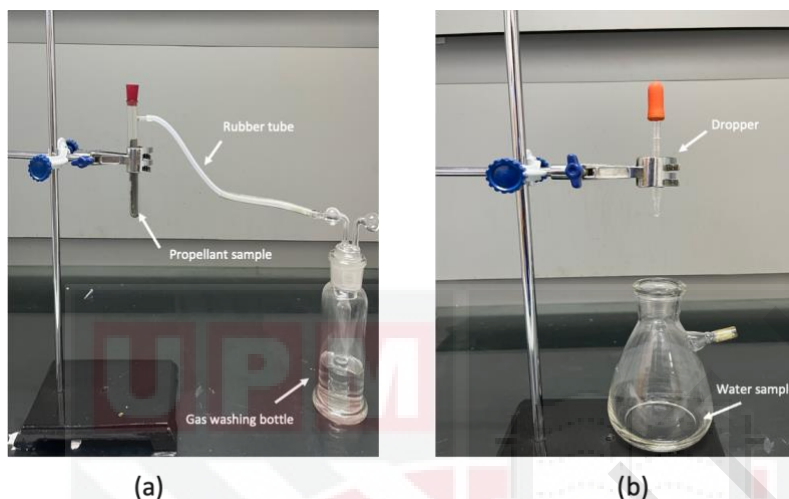


Figure 3.10: Experimental setup of (a) Gas bubbling setup and (b) Mohr's titration

The methodology for calculating the chloride content in the water sample was as follows. The initial stage involved filling the dropper pipette with 5 ml of 0.1 molar silver nitrate (AgNO_3) solution using a glass funnel. Next, a 10 ml water sample, as in Figure 3.11 (a), was poured into a conical flask, and 2-3 drops of 0.25 molar potassium chromate (K_2CrO_4) solution were added. Next, the water sample underwent titration with AgNO_3 solution by gradually adding the silver nitrate solution from the dropper pipette. This will change the colour of the K_2CrO_4 to a yellowish milky colour, as referred to in Figure 3.11 (b).

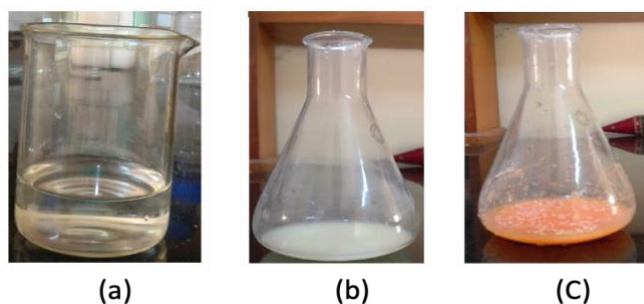


Figure 3.11: Color references of (a) water sample, (b) midpoint titration, and (c) end-point titration

(Source: Vellaisamy et al., 2020)

The conclusion of the titration began with the emergence of a reddish-brown precipitate, as in Figure 3.11 (c), and the measurement of the volume of AgNO_3 solution used in the dropper pipette was recorded. The technique was replicated three times to obtain the average result. Based on Hamim et al. (2023), the first calculation is to determine the chloride ion using the formula:

$$M_1V_1 = M_2V_2 \quad (26)$$

Where M_1 is the molarity of AgNO_3 , V_1 is the volume used in the dropper pipette, M_2 is the molarity of the water sample, and V_2 is the volume of the water sample. The chloride content in the water sample is determined by using the following formula:

Chlorine content (ppm):

$$\text{molarity of water samples } (M_2) \times 35.5 \times 1000 \quad (27)$$

Where 35.5 is the molar mass of HCl (Doll et al., 1992). The method mentioned above is performed for every water sample containing dissolved propellant exhaust gases to determine the chloride content of each propellant sample.

Each sample was subjected to three titrations, and the chloride content was calculated for each titration to calculate the average value. This is due to aleatory uncertainty, which is due to data limitation and sample variability. The result data on the samples' chloride content in ppm has been tabulated.

3.5.2 Uniaxial Tensile Test of Composite Solid Propellant (CSP) Grain

As composite solid propellant (CSP) is a type of fuel in the solid state, the mechanical properties of the solid structure and integrity must be evaluated when a novel formulation is made. This is because these systems' safety and reliability are paramount, as mechanical properties testing helps evaluate solid propellants' strength, durability, and behaviour under various conditions, which is crucial for designing safe and reliable propulsion systems. Besides, the mechanical properties, specifically the propellant's tensile strength, affect its ability to withstand the internal pressures and forces generated during combustion. By characterising these properties, researchers can improve performance, burn rate, and efficiency. Therefore, uniaxial tensile testing is used to determine novel CSP's tensile and strength properties with KMnO_4/AP as a dual oxidiser.

The uniaxial tensile test was conducted using the Shimadzu Universal Testing System in accordance with the JANNAF standard specimen for CSP samples, as in experimental works done by Kim et al. (2019). Figure 3.12 (a) shows the setup for the uniaxial tensile test, and Figure 3.12 (b) shows the environmental chamber used to vary the temperature conditions when running the samples. The temperature in the environmental chamber varied from 20°C, 30°C, 40°C,

50°C, and 60°C where this parameter value was also according to the experimental works done by (Kim et al., 2019). This parameter is very important in studying the tensile strength properties of CSP because the tensile strength of CSP can be influenced by temperature, as higher temperatures can weaken the polymer binder, reducing its ability to hold the propellant together. This can result in a lower tensile strength at elevated temperatures. So, by varying the temperature, the more realistic mechanical properties of the actual applications can be achieved (Garino et al., 2021).

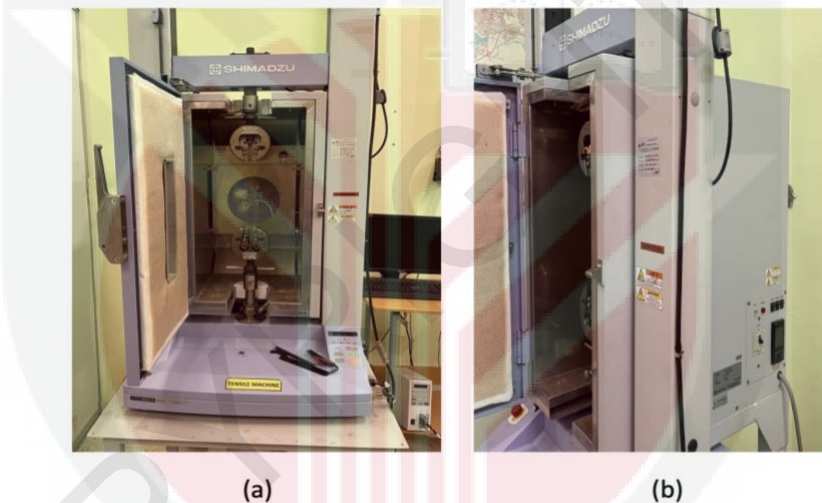


Figure 3.12: Test set-up for (a) the uniaxial tensile test and (b) the environmental chamber

For the preparation of carrying out the tests, 39 dog bone samples of propellant were fabricated with the size of 25.4 mm (H) x 120 mm (L) x 12.7 mm (W), as illustrated in Figure 3.13. All propellant samples were produced according to the formulations mentioned previously with the same curing condition, and the sample design matrix of uncoded values for the factors is given in Appendix A1. The propellant blocks were clamped to the sample

clammer at the top and bottom, as shown in Figure 3.14 (a). Then, the strain gauge, as in Figure 3.14 (b), was attached at the centre of the dog bone propellant sample.



Figure 3.13: Propellant dog bone sample according to JANNAF standard specimens

Strain gauges should be placed in locations where strain is expected to be high and appropriately aligned according to the anticipated direction of strain during loading. Before conducting the actual test, the strain gauge is calibrated to ensure accurate measurements. This is because the epistemic uncertainty on the sensor or strain gauge must be avoided and overcome. The measurement data might not be consistent and will lead to a strain measurement error. This involves applying known loads or strains to the sample and recording the output signals from the strain gauges. Next, the temperature in the environmental chamber was set to the desired value, and the chamber door was locked to prevent the environmental error of losing the desired temperature. All the samples were run at a 10 mm/min sample strain

rate, and the elongation value and stress-strain curve were plotted on each sample to get the tensile strength properties.

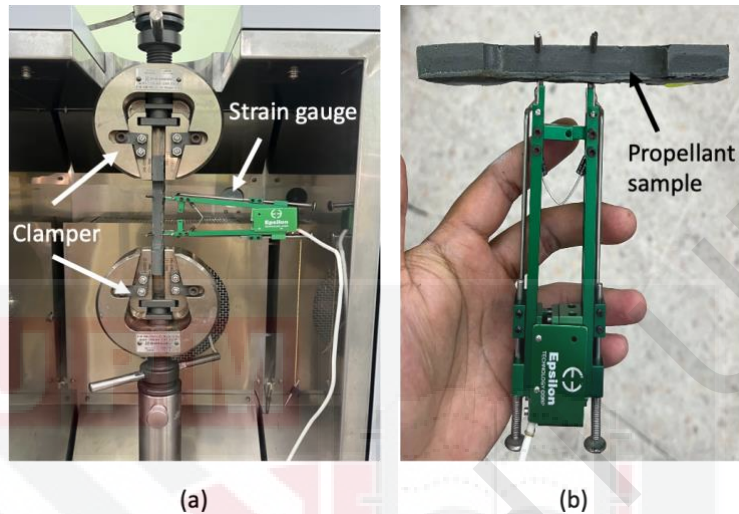


Figure 3.14: Sample preparation setup on tensile testing machine (a) sample clamping (b) strain gauge attachment to the dog bone propellant samples

3.5.3 Burn Rate Analysis of Composite Solid Propellant (CSP) Sample

The burn rate test is one of the most vital analyses in composite solid propellant CSP as it will give data on the propellant sample's burning behaviour performances. Besides, this is a common type of testing in investigating the novel catalyst in the CSP formulation and composition. In this study, the burn rate test was performed to elucidate the effect of KMnO_4/AP as a dual oxidiser in an AP-based CSP system with different ratios. The burn rate testing was conducted using the Crawford strand burner setup, which was developed by Universiti Putra Malaysia. It involves burning a small propellant strand in a controlled environment while measuring the time it takes for the strand to burn over a certain length. Besides, this Crawford strand burner

setup was the first version made by Universiti Putra Malaysia and is considered a low-pressure strand burner setup. It can go up until 3 atm and is controlled by the relief valve at the end cap. Figure 3.15 (a) shows the experimental setup of the Crawford strand burner test, and Figure 3.15 (b) illustrates the sample holder attached to the cap.



Figure 3.15: Crawford type strand burner setup (a) close-up view on the pressure gauge and sample holder setting and (b) full view

39 Propellant strand samples of $6\text{mm} \times 6\text{mm} \times 150\text{mm}$, as shown in Figure 3.16 (a), were fabricated according to the formulation given previously, and each of the formulations was prepared in 3 samples, which is the same as the experimental conducted by (Sangtyani et al., 2019). Besides, the sample design matrix of uncoded values for the factors is given in Appendix A2. Figure 3.16 (b) illustrates the sample of propellant strands prepared for all samples. The procedure required igniting propellant strands using nichrome ignition wire within a chamber bomb pressurised with nitrogen gases. The propellant strands were wrapped in nichrome wire connected to the electrical contact pyrotechnic connector. The burning of the propellants was done in low-

pressure conditions with varying pressures of 1, 1.5, 2, 2.5, and 3 atm. This value is the same as that of experimental work done in low-pressure conditions by Hafizi et al. (2017). Following the reference in Kou et al. (2024), nitrogen is used to pressurise the firing vessel and a relief valve control and maintains the pressure inside the chamber. During the test, the chamber pressure increased moderately due to increased hot gases from combustion and heat released. Besides, according to Jain et al. (2019), solid propellant burn rate testing is conducted at different pressures to understand how the burn rate of the propellant behaves under various environmental conditions and to ensure the safe and effective performance of solid rocket motors.



Figure 3.16: Propellant strands samples for burn rate test of composite solid propellant

The strand is electrically ignited at one end. The strands are usually inhibited along their length to ensure that burning only occurs perpendicular to the surface. The burn rate is obtained by measuring the time for the propellant strand samples to burn entirely with length. The total length of the propellant strand used to calculate the burn rate regression is only 90mm, whereas the

other 60mm is used to attach the propellant in the sample holder, as shown in Figure 3.17.



Figure 3.17: Propellant strand sample attached to the sample holder

Experiments were repeated 3 times to obtain 3 burning rate readings at each pressure and formulation, establishing the repeatability of the burning rate values. According to Sangtyani et al. (2019), the burning rate was typically determined by three strands at a single pressure level, and repeatability of the burning rates was noted within 5%, which is acceptable. Moreover, this experiment sample size was designed using response surface methodology to get the optimum contour plot of the data result. The burn rate (mm/s) versus pressure was plotted for all the sample formulations were calculated using the following formula:

$$r = L_p / t_p \quad (28)$$

Where:

r = Burn rate of propellant, (mm/s)

L_p = Propellant length, (mm)

t_p = Propellant burning time, (s)

Due to manually measuring the time taken for the propellant to burn completely, some sensitivity error must be taken. The sensitivity value taken is 1/1000. However, the burning time is taken to 1/100, considering a worst-case condition as per an experiment conducted by Aziz et al. (2013). Moreover, due to the blurry surface of the pressure chamber made of acrylic coated with glass fibre epoxy composite, the repeated burning of the propellant sample is important in getting constant data results. This type of aleatory uncertainty error comes from human error and sample variations. The result data from the burn rate testing will be tabulated and analysed to calculate the mass flow rate using the equation (18). This mass flow rate gives a clear qualitative value on the effect of CSP burn rate results on the rocket motor's performance, specifically on the thrust value production.

3.6 Design of Experimental (DOE) and Analysis Steps

This work used a two-step experimental methodology to create a model for the tensile strength and burn rate properties of the KMnO_4/AP as a dual oxidiser in a CSP system. This is because these two tests consist of more than two manipulated factors or variables, while the characterisation and the other testing will have only one factor. Designing experiments for the experimental analysis is crucial if the factors are more than two. The series of designs used in the experiment will be discussed in this chapter. The first series of studies

was called the screening process, and it used a factorial design (FD) to reduce the number of components by identifying a few essential primary effects and distinguishing them from the many less important ones. After the key factors were identified, the second stage, known as the optimisation process, was carried out using the response surface methodology (RSM). RSM was used to optimise the responses and estimate the interaction of components, including quadratic effects, which were then utilised to predict the form of the response surface. This was followed by an optional validation step to verify the accuracy of the prediction model based on the responses. The average difference in percentage between the experimental and computed results for each response determines the prediction model's accuracy.

3.6.1 Factorial Design (FD) Method Approach in The Research Work

Figure 3.18 shows the flowchart for factorial design (FD). This statistical approach began with determining the significant factors such as temperature condition, ratio of KMnO_4 to AP, chamber pressure, and levels based on fundamental laboratory work or information from the literature review. Responses such as tensile strength for the uniaxial tensile test and burn rate value for the burn rate test were selected. MINITAB, a statistical software, was utilised to generate a table of experiments to be experimented. Data results obtained from experiments were inserted in the MINITAB software under the response column and then analysed.

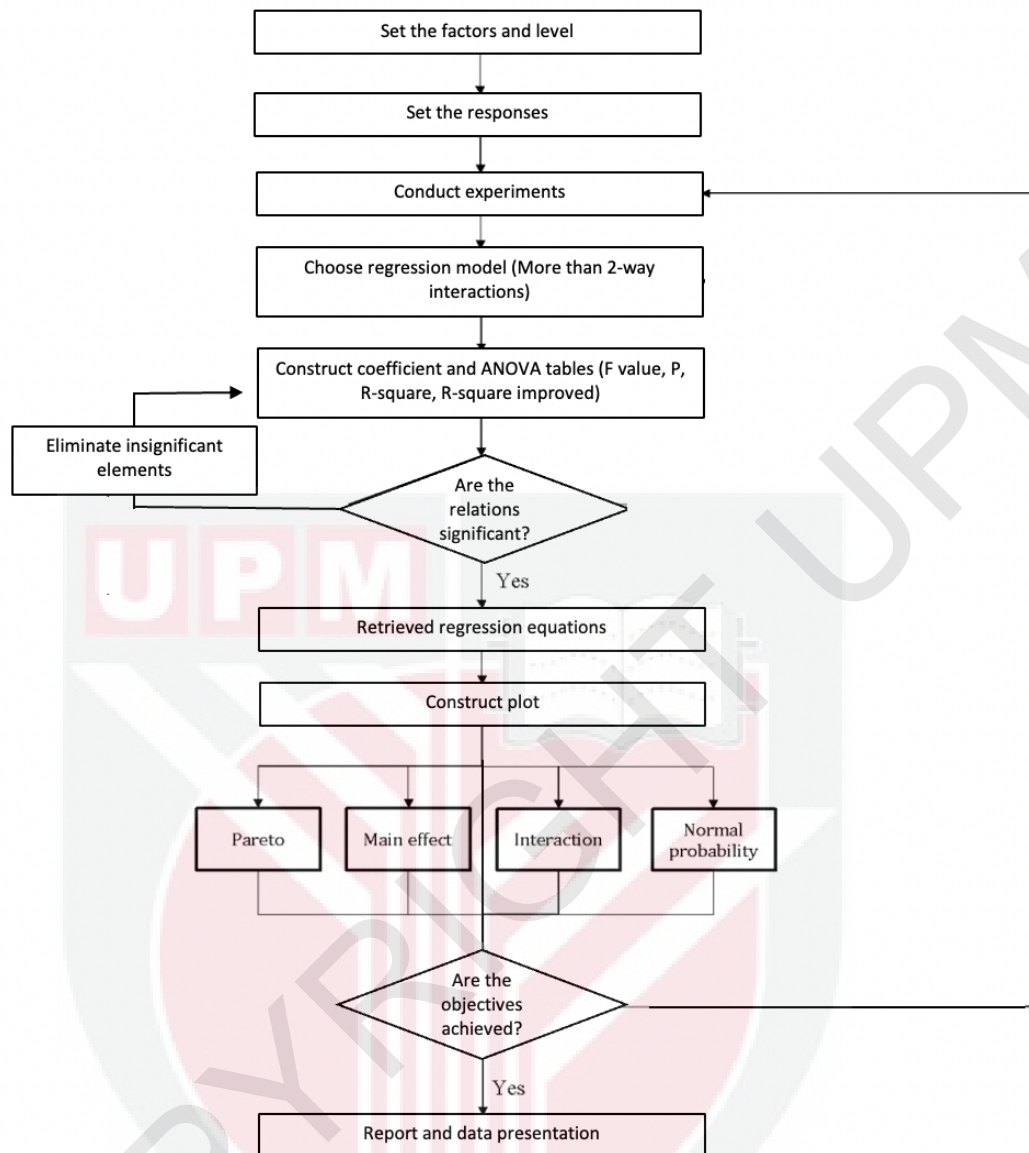


Figure 3.18: Overall flowchart process of factorial design

A regression model with up to two-way interactions was chosen in this study. There was no relevance to using higher-order interaction. The ANOVA and estimated effect and coefficient (EEC) tables displayed the results. The difference between the responses of two levels (high and low level) of components is represented by the net effect from the EEC table. The net effect was divided into two parts to get the regression coefficient. According to

Roslan et al. (2024), the standardised effect can be computed by dividing the regression coefficient by the standard error of the coefficient.

One of the criteria for identifying the best-fitting model was to examine the P value, which significantly affected the model. When the factor or interaction P value was less than 95.00%, it was considered significant ($P = 0.050$). According to Rosly et al. (2019), larger R^2 values result in more effective coefficient determination of the regression equation. The modest difference between R^2 and adjusted R^2 suggests that the model best fits the response. The F value obtained from the ANOVA table quantifies the extent to which the factors account for the variability in the data relative to their mean. According to Wang et al. (2014), a higher F value indicates a higher level of confidence in the factors' ability to explain the variation in the data concerning their mean appropriately. This suggests that the estimated factor effects are genuine. Despite their lack of significance ($P > 0.050$), the main terms (factors) were not deleted. Only interaction terms that do not exhibit statistical significance will be excluded. After eliminating all deemed unimportant interactions, the data will be subjected to further analysis. Subsequently, a predicted regression equation will be developed based on the results obtained from the EEC table. The regression equation constructed using MINITAB indicated the impact of various factors on the projected replies. Additionally, it was used to predict the optimum condition to achieve desired goals such as high tensile strength and high burn rate.

Four plots, which are pareto, main effect, interaction, and normal probability plots, were created for additional analysis. The Pareto plot is a valuable tool for determining the significance and size of main and interaction effects. A reference line is drawn in the plot to show that any term (factor) that goes beyond it may be significant. The MINITAB program automatically draws the reference line at the error margin (ME). The ME is determined using the pseudo-standard error (PSE) formula, $ME = t \times PSE$, where $t = (1-\alpha/2)$ and $\alpha = 0.05$. Because the reference line is set at the mean error of the data, any value below it is regarded as a random statistical error, but those above it are seen as meaningful.

The horizontal line on the main effect plot indicates the average compressive strength for all runs, and the mean response values between five levels of a factor are produced. An interaction plot is a graphical tool that displays the effect of every potential combination of factors on the answer. Because it illustrates the link between two parameters, this plot is significant. There is an interaction between the two components if the two lines do not intersect or are not parallel to one another. The normal probability plot is a graphical method for determining if data collection is usually distributed. When all the plot points lie on a straight line, the data is said to be normally distributed (Asadollahzadeh et al., 2014). The subsequent subsections describe the experimental design based on each test. The five-level factorial: full factorial was used in the experiment's design as the total number of factors is two, and the replicates are three, which is less than four.

3.6.1.1 Factorial Design (FD) Method for Uniaxial Tensile Test and Analysis

Two factors that could significantly affect the responses (tensile strength value) were chosen based on previous literature. The factors were temperature conditions and the ratio of KMnO_4 to AP. The five levels with coded and uncoded levels and values used in this experimental work are shown in Table 3.3. MINITAB assigns a value of -2 to the low level of all factors, +2 to the high level, and 0 to the centre points. With coded units, it can compare the coefficient sizes (on a standard scale) to ascertain which element affects the result the most. MINITAB always utilises coded units for analysis, independent of how the design is shown. In an experimental study by Kim et al. (2019), the maximum temperature condition for performing a uniaxial tensile test is up to 60°C . This varies in temperature up to 60°C , resulting in a very precise tensile strength value that complies with the actual application condition of CSP. Besides, the variation value ratio of KMnO_4 to AP is followed by the experiment conducted by Tagliabue et al. (2016), in which they evaluate the performance of AN/ADN as a dual oxidiser for CSP.

Table 3.3: Coded and uncoded factor values of uniaxial tensile test

Factor	Notation	Coded level	Uncoded values
Temperature condition	V_1	-2, -1, 0, 1, 2	20°C , 30°C , 40°C , 50°C , 60°C
The ratio of KMnO_4 to AP	V_2	-2, -1, 0, 1, 2	0:100, 20:80, 40:60, 60:40, 80:20

In this design of experiment, the total based runs are 13. However, the three replications were considered thus with a total of 39 experimental runs. Since the number of experimental runs was low and the number of factors considered was less than four, FD must be used. The experimental design for RSM for both coded and uncoded factors is given in Appendix A3.

3.6.1.2 Factorial Design (FD) Method for Burn Rate Test and Analysis

Similar to the uniaxial tensile test, two factors that may potentially affect the response (burn rate value) were considered. The factors were chamber pressure and the ratio of KMnO_4 to AP. The coded and uncoded values of the factors are shown in Table 3.4. Based on the previous literature study, the 3 atm chamber pressure value is the maximum value chosen. The rocket propellant grain will undergo varying pressure inside the rocket motor chamber during combustion (Park et al., 2019). According to the CSP application, the variety of chamber pressure values is vital in this burn rate study to get a better value.

Table 3.4: Coded and uncoded factor values of burn rate test

Factor	Notation	Coded low level	Uncoded low values	Coded high level	Uncoded high values
Chamber pressure	V_1	-2	1 atm	+2	3 atm
Ratio of KMnO_4 to AP	V_2	-2	0:100	+2	80:20

A five-level factorial: Factorial design gave a total number of 39 experimental runs. This number is the same as the uniaxial tensile test experimental design

previously. The base run in this experimental design is 13, but with three replicates on each sample, the total number of runs would be 39. This means the total number of 39 was sufficient to study the two-way interactions for two factors at five levels. The experimental design for RSM for both coded and uncoded factors is given in Appendix A4.

3.6.2 Response Surface Methodology (RSM) as Experimental Analysis Modelling

As mentioned in the previous chapter, a response surface design refers to a collection of sophisticated design of experiments (DOE) methodologies that facilitate a more profound comprehension and optimisation of the response variable. In this study, the central composite design (CCD) was selected as the preferred approach for the RSM, as opposed to the Box-Behnken design. While the middle point is crucial for determining the optimal position of the factors, as illustrated by a curved line, the model, particularly the quadratic model when using the Box-Behnken design, lacks significant control. The CCD was selected due to its ability to offer more comprehensive insights into the function inside the experimental region and its shown predictive capabilities, as documented in prior scholarly works. The number of experimental runs required for an RSM study depends on several factors, including the number of factors and their levels. Table 3.5 shows a comparison between conventional design and RSM, with 5-level factors for 1 repetition per sample. To calculate the number of experimental runs required for a conventional method and RSM study based on the levels and factors, the following formula can be used:

Conventional method:

$$N = L^k \quad (29)$$

Where N is the total number of experimental runs, L is the level, and k is the number of factors.

RSM:

$$N = (2k + 2k + P) \quad (30)$$

Where $P = 2^k$, N is the total number of experimental runs and k is the number of factors.

Table 3.5: Comparison of total number of experiments run between the conventional method and RSM

Factors	Level	Conventional method	RSM
2	5	$(5^2) = 25$	$(2*2 + 2*2 + 2^2) = 12$

With two factors, the conventional method requires 25 experimental runs, while RSM only requires 12 runs to complete the same experiment. RSM is relatively more beneficial and advantageous in design with two or more than two factors. The flowchart of RSM can be illustrated in Figure 3.19. The initial phase is like the FD flow process except for two steps, which are (i) the determination of the value of $\alpha = 2$, which was applied throughout the study, and (ii) the selection of three different regression models. It is important to consider three distinct types of regression models, namely linear, square, and interaction. The comprehensive regression model equation is crucial in determining two key aspects: (i) establishing the significant association

between factors and (ii) estimating the optimal value. Due to the lack of knowledge regarding the optimal location at the start of RSM studies, it is logical to employ a rotatable design that can consistently deliver accurate estimation at all points equidistant from the design centre (Chaudhary et al., 2021).

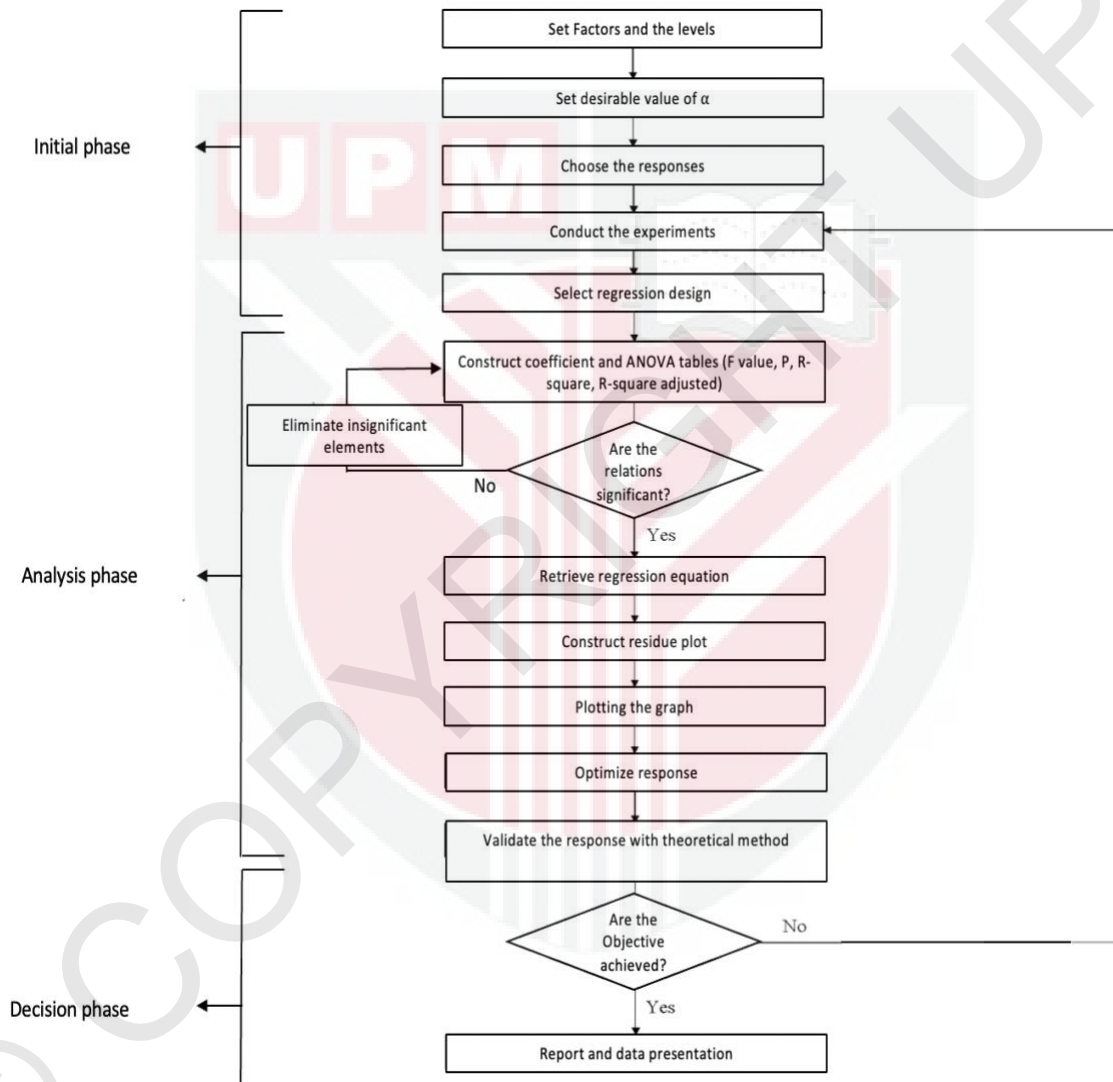


Figure 3.19: Flow chart of RSM used in this study

After selecting and analysing each regression model, unimportant terms were removed. Subsequently, the software created the EEC table and ANOVA

table. The preceding table provided a comprehensive overview of the coefficients for all terms included in the model. In contrast, the subsequent table summarised the linear, square, and interaction terms. Except for the primary terms, all other deemed insignificant terms were removed, and the data was analysed again. As stated by Roslan et al. (2024), employing a simplified model consisting of just significant terms has the potential to enhance the accuracy of the predictors in situations where the objective is to identify the ideal configurations of crucial components. However, since this study only involves 2 factors and not exceeding 4 factors, all factors will be used in RSM to analyse and obtain the result data.

The final step in the modelling process is experimental validation, which tests the precision and reproducibility of the regression and RSM models produced. Under the optimal settings derived from the optimisation plot, three validation experiments were conducted. Sivaraos et al. (2014) assert that in the context of a nonlinear process, the confirmation of model optimisation and validity is contingent upon the attainment of an average difference between experimental and predicted values that is below 15%. The subsequent subsections describe the experimental designs corresponding to each individual test.

3.6.2.1 Response Surface Methodology (RSM) for Uniaxial Tensile Test and Analysis

Both factors, which are the ratio of KMnO_4 to AP and temperature conditions, will be used in this testing and designated as V_1 and V_2 , respectively. The levels for each factor and their ranges are shown in Table 3.6. The desired

responses were the tensile strength, which was assumed to be influenced by these two factors, and the stress versus strain and elongation curve will be plotted. The design matrix for both coded and uncoded factors is given in Appendix A5.

Table 3.6: Factors and levels used for uniaxial tensile test

Factors	Unit	Notation	Levels				
			-2	-1	0	1	2
KMnO ₄ : AP ratio	-	V ₁	0:100	20:80	40:60	60:40	80:20
Temperature condition	°C	V ₂	20	30	40	50	60

3.6.2.2 Response Surface Methodology (RSM) for Burn Rate Test and Analysis

The two factors used, the ratio of KMnO₄ to AP and chamber pressure, were designated as V₁ and V₂, respectively. The observing parameter is burn rate value along with chamber pressure, and the curve was plotted for analysis. The levels of the two factors and their working ranges are shown in Table 3.7.

Table 3.7: Factors and levels used for burn rate test

Factors	Unit	Notation	Levels				
			-2	-1	0	1	2
KMnO ₄ : AP ratio	-	V ₁	0:100	20:80	40:60	60:40	80:20
Chamber pressure	atm	V ₂	1	1.5	2	2.5	3

3.7 Summary

The methodology and procedures and the sample specifications of each of the experimental works have been elaborated in this section. The KMnO₄/AP dual

oxidiser was synthesised using the agate mortar method and characterised in terms of physical, morphological, elemental composition, crystallinity, surface area, molecular interaction, and thermal properties. The dual oxidiser was then incorporated into the CSP system using manual propellant mixing through the kneading mixer. The CSP samples were characterised by physical, morphological, elemental composition, and thermal properties. Next, the performances regarding chlorine concentration, tensile strength properties, and burn rate behaviour were elucidated. The chlorine concentration test was determined using Mohr's titration method, the tensile strength properties were investigated using the uniaxial tensile test, and the burn rate behaviour of the propellant sample was measured using Crawford strand burner type. Both experimental works of uniaxial tensile test and burn rate behaviour of the propellant sample were designed through RSM due to the existence of the two factors.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Overview

The dual oxidisers potassium permanganate (KMnO_4) and ammonium perchlorate (AP) were synthesised using an agate mortar, which was then integrated into the AP-based composite solid propellant (CSP) for testing and analysis. The results of the experiment are explained in detail in this chapter. The research study's testing and analysis were divided into two sections, which are the characterisation and testing of the KMnO_4 /AP dual oxidiser and the characterisation and testing of the AP-based CSP. The KMnO_4 /AP dual oxidiser's morphological structure and elemental composition were examined using a scanning electron microscope (SEM) and energy-dispersive X-ray analysis (EDX). Besides, the crystallinity properties and molecular interaction were examined through X-ray diffraction (XRD) and RAMAN spectroscopy, respectively. The specific surface area was evaluated using Brunauer–Emmett–Teller (BET), and the pore volumes and pore size distributions were determined from the adsorption branches of isotherms. Additionally, the effect of AP thermal decomposition on KMnO_4 behaviour was investigated using differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA).

The SEM and EDX methods were utilised for AP-based CSP to observe the microstructural and elemental composition. Then, the HCl concentration test was conducted using Mohr's Titration method. The heat of combustion and burn tests for the propellant samples were performed, and the resulting data

were analysed and discussed in this chapter. In addition, uniaxial tensile testing was employed to observe the tensile strength properties of the propellant samples. All data from these tests were presented in this chapter, including contour plots derived from the response surface method (RSM) for the burn rate and uniaxial tensile testing results.

4.2 Dual Oxidiser KMnO_4/AP Characterizations

Before initiating the fabrication process of CSP, the dual oxidiser consisting of KMnO_4/AP was prepared. This step is crucial for understanding the synthesised products of dual oxidisers' physical characteristics, morphological structure, elemental composition, surface area analysis, chemical bonding, and thermal properties.

4.2.1 Physical Observation of AP, KMnO_4 , and Dual Oxidiser KMnO_4/AP

The process of mixing using an agate mortar did not change the physical characteristics of the AP and KMnO_4 . Furthermore, due to the crushing and grinding process, the AP is well mixed with KMnO_4 , and there is a change in the colour of KMnO_4/AP with different ratios. Figure 4.1 shows the physical behaviour of AP, KMnO_4 , and KMnO_4/AP powder with different ratios.

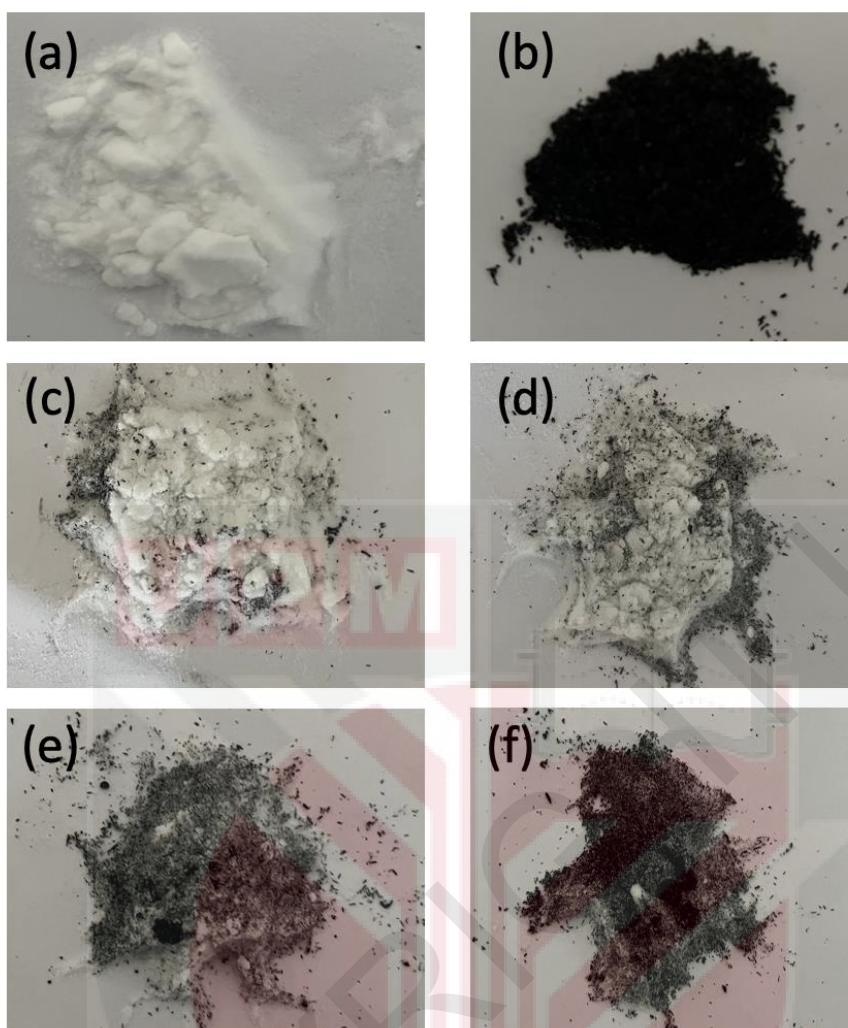


Figure 4.1: Physical condition of the sample of AP and KMnO_4 and KMnO_4/AP dual oxidiser with different AP to KMnO_4/AP ratios

In Figure 4.1 (a), the AP sample exhibited typical physical characteristics, appearing as a white crystal. At the same time, KMnO_4 was observed as a dark purple, almost black, crystalline solid, as in Figure 4.1 (b). Additionally, the crystals typically have a granular or rod-like shape. It is observed that the scattered dark purple colour of KMnO_4 powder is observed in KMnO_4/AP with a ratio of 20:80, as in Figure 4.1 (c). As the ratio of KMnO_4 to AP increased to 40:60 and 60:40, the colour of the mixture gradually darkened, as in Figure 4.1 (d) and Figure 4.1 (e) change attributed to the dominance of KMnO_4 , which

appeared as a dark purple, ensuring the colour changes were consistent throughout. Besides, the appearance of the white crystal of AP has 90% faded since the ratio of KMnO_4 to AP is at 80:20, and the dark purple with rod-like particles is observed to be dominant, as in Figure 4.1 (f). Particles also tended to agglomerate or clump together, potentially forming larger structures during the mixing process, especially in the case of AP. An agate mortar effectively broke down these agglomerates, resulting in a more dispersed and uniform mixture. Crushing the particles using the agate mortar likely initiated mechanical bonding between KMnO_4 and AP. According to Mukherjee et al. (2022), the crushing and grinding of the particles using agate mortar can initiate the mechanical bonding between two elements mixed via several physical interactions and processes. This interaction includes particle size reduction, increased surface contact, mechanical interlocking, and surface energy changes. The detailed observation of these binding characteristics was discussed in the following subchapter using morphological analysis through SEM.

4.2.2 Morphological analysis of AP, KMnO_4 , and dual oxidiser KMnO_4/AP

Using SEM examination, the morphology of AP, KMnO_4 , and KMnO_4/AP samples were examined, as can be seen in Figure 4.2. The AP structure depicted in Figure 4.2 (a) predominantly exhibited a monoclinic form, with its crystals being prismatic or tabular shapes, similar to the findings of McClain et al. (2020). The average particle size of these samples ranged from approximately 100-120 μm . In Figure 4.2 (b), KMnO_4 appeared as long,

slender needles or prisms. These rod-like structures result from the orthorhombic crystal lattice (Bian et al., 2021). As mentioned before, the KMnO_4 crystals were characterised by a deep purple or almost black. This intensely purple colour signified the compound's strong absorption in the visible electromagnetic spectrum (Abisha et al., 2023).

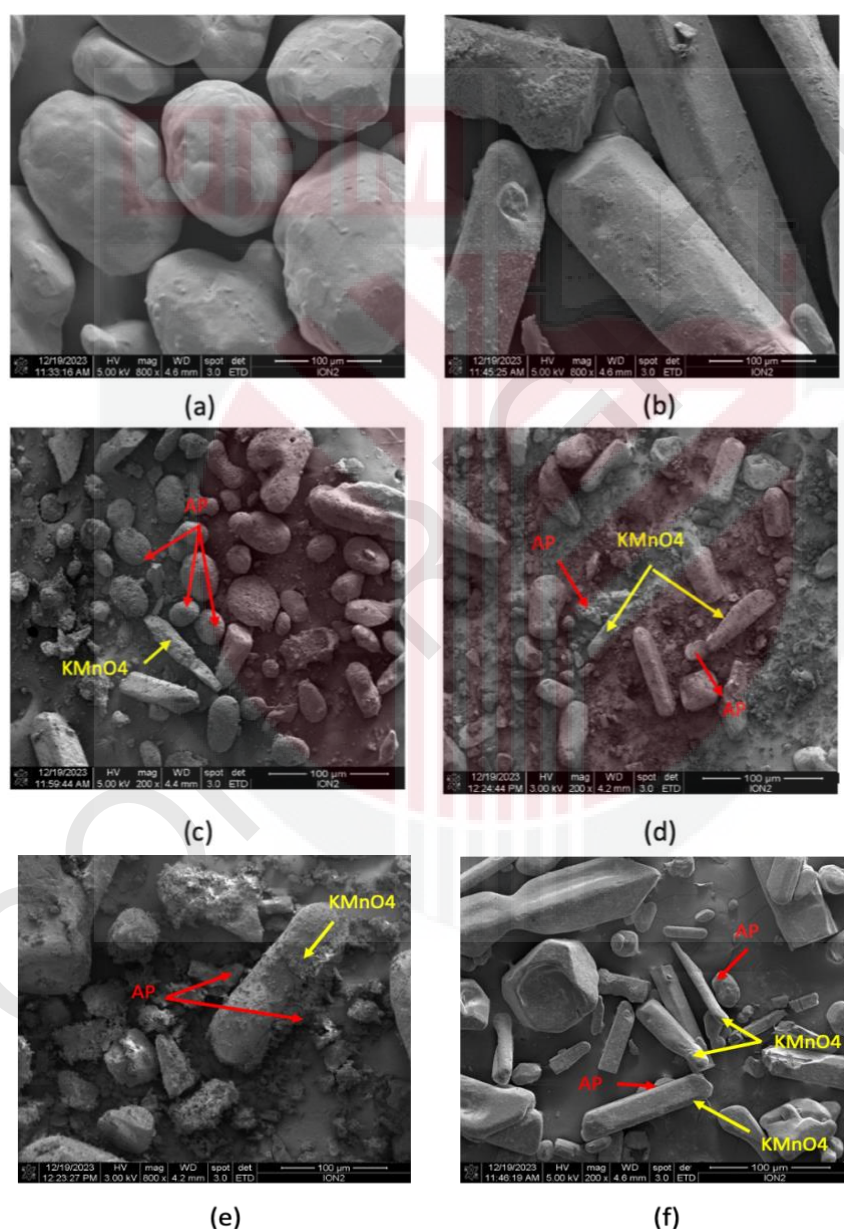


Figure 4.2: FESEM morphology of (a) AP, (b) KMnO_4 , (c) KMnO_4/AP (20:80), (d) KMnO_4/AP (40:60), (e) KMnO_4/AP (60:40), and (f) KMnO_4/AP (80:20) after dry for 1 hour

Based on Figure 4.2, both AP and KMnO_4 particle sizes exhibited a significant reduction, with the average particle size ranging from 20 to 50 μm . The size reduction, mainly caused by crashing, led to a smoother surface particle size of AP and KMnO_4 , increasing bondable surface area. As the particles decrease in size, the proximity between AP and KMnO_4 particles rises, facilitating intimate contact to form a noticeably new structure, as in Figure 4.2 (c). AP started to adhere to the KMnO_4 surface, resulting in a structure with different crystallinity, as indicated by the yellow and red arrows. This attachment of AP particles to the surface and edges of the KMnO_4 indicated mechanical adhesion. Mechanical grinding causes deformation and microfractures in both AP and KMnO_4 crystal structures, as seen in Figure 4.2 (d). These flaws can generate high-energy sites that are more susceptible to bonding.

Mucsi et al. (2019) claimed that grinding generates mechanical activation, whereby the elevated surface energy of the particles resulting from the grinding process enhances their reactivity and mechanical bonding ability. In addition, this increases the likelihood of adhesive interactions among the particles, including van der Waals forces (Ilyushchenko et al., 2018). In Figure 4.2 (e), the AP particles start to scatter from each other and adhere closer to the KMnO_4 rod. Moreover, the attachment of AP to the KMnO_4 surface reduced particle agglomeration, as in Figure 4.2 (f), thereby increasing the specific surface area, which, in turn, enhances its thermal properties because the reactivity is increased. This increase in specific surface area was further discussed through BET analysis in section 4.2.6.

4.2.3 Elemental Composition Analysis of AP, KMnO_4 , and Dual Oxidiser KMnO_4/AP

The EDX spectra of AP, KMnO_4 , and KMnO_4/AP at various ratios were analysed to study the surface chemical composition. Figure 4.3 and Figure 4.4 depict the corresponding mapping results, while the elemental composition percentages were tabulated in Table 4.1. For AP, based on Figure 4.3 (a), the primary elements detected through EDX included nitrogen (N), hydrogen (H), chlorine (Cl) and oxygen (O). The perchlorate ion (ClO_4^-) contains chlorine and oxygen, whereas nitrogen and hydrogen are the ammonium ion (NH_4^+) constituents. McClain et al. (2020) confirmed that hydrogen cannot be detected in EDX due to its low atomic number. Moreover, oxygen was found to be the dominant element in AP, with a weight percentage of 64.52%, in contrast to chlorine (Cl), which has a weight percentage of 35.48%. This indicates that AP is rich in oxygen compounds, making it a potent oxidiser in combustion. The percentages of chlorine and nitrogen were nearly identical, with values of 24.12% and 22.10% respectively. In Figure 4.3 (b), potassium (K), manganese (Mn), and oxygen (O) elements were detected in KMnO_4 . KMnO_4 is composed of potassium cations (K^+) and permanganate anions (MnO_4^-), with manganese having the highest element composition at a weight percentage of 38.17%, followed by potassium and oxygen with percentages of 36.81% and 25.02%, respectively. This highest value contradicts the physical characteristics of KMnO_4 , in which the colour is dark purple. Figure 4.4 illustrates the EDX spectra of KMnO_4/AP with different KMnO_4 to AP ratios.

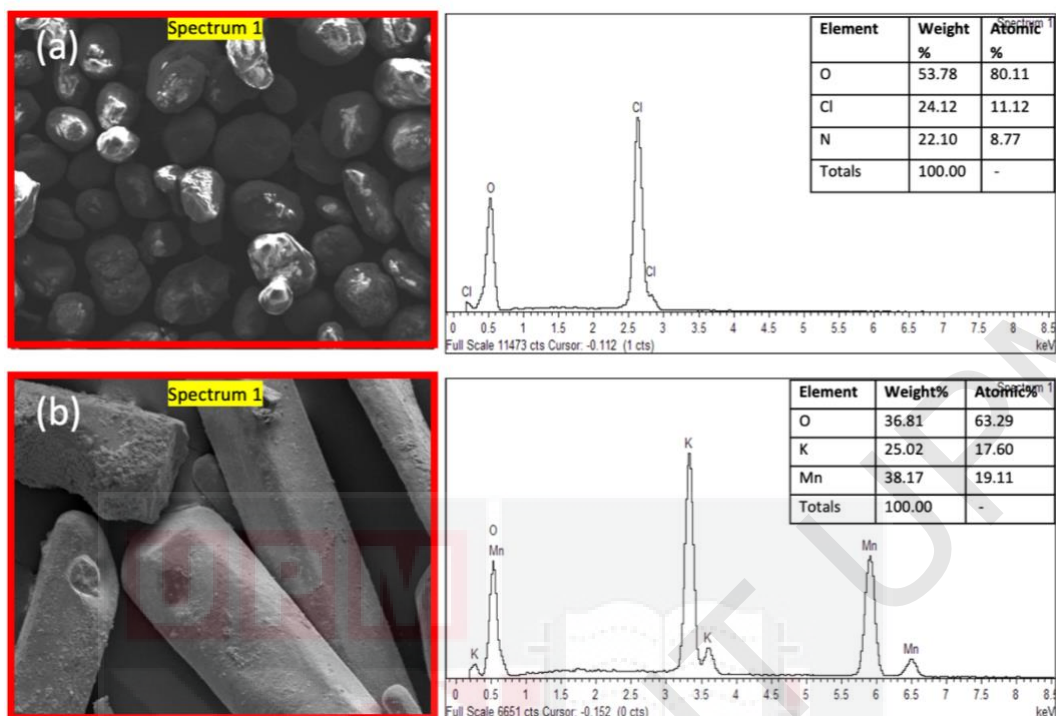


Figure 4.3: EDX and mapping of (a) AP and (b) KMnO_4

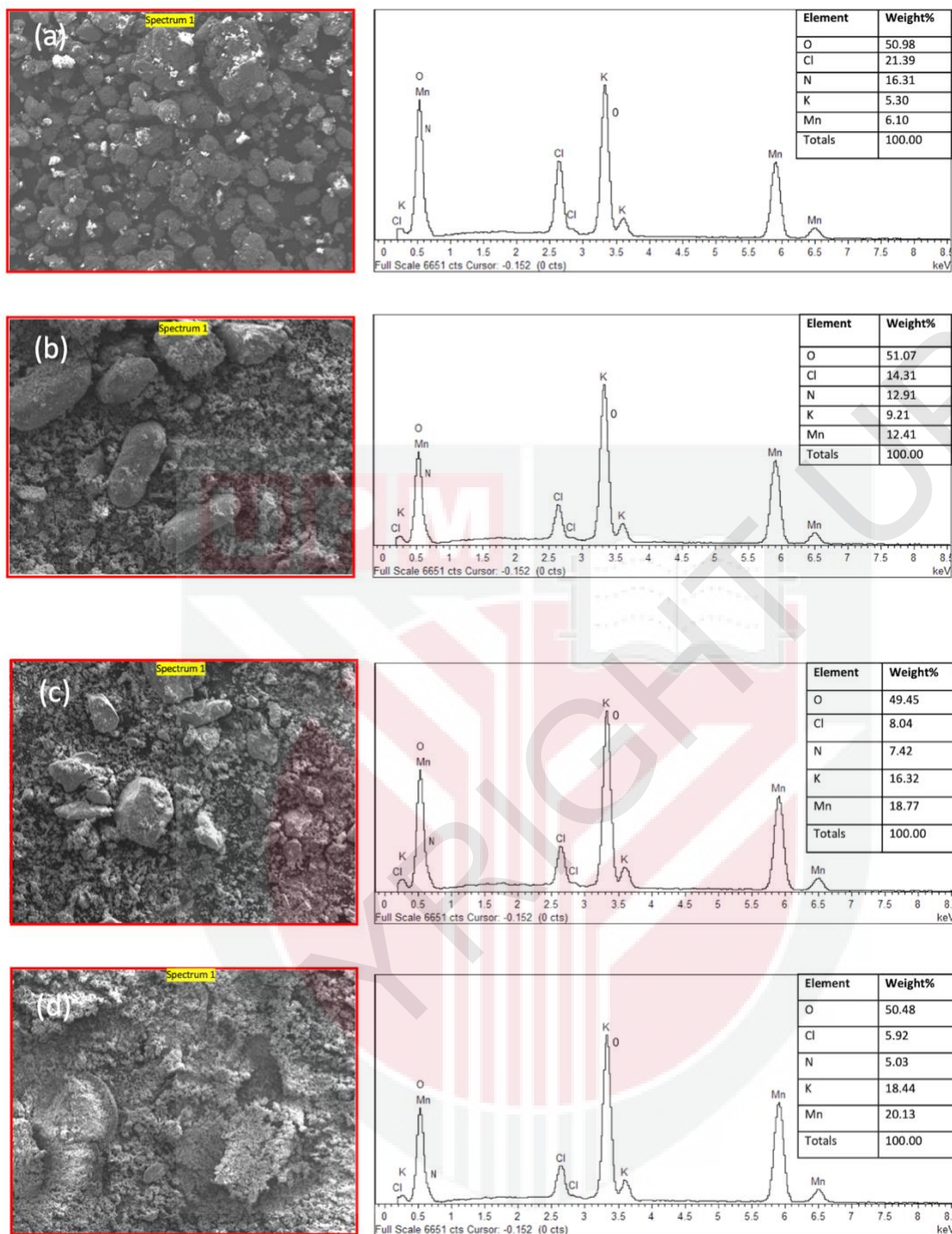


Figure 4.4: EDX and mapping of (a) KMnO_4/AP (20:80) (b) KMnO_4/AP (40:60) (c) KMnO_4/AP (60:40) and (d) KMnO_4/AP (80:20)

Table 4.1: Elemental composition percentage of all the samples from EDX result analysis

Element	AP	KMnO ₄	KMnO ₄ /AP (20:80)	KMnO ₄ /AP (40:60)	KMnO ₄ /AP (60:40)	KMnO ₄ /AP (80:20)
O (wt.%)	53.78	36.81	50.98	51.07	49.45	50.48
N (wt.%)	22.10	-	16.31	12.91	7.42	5.03
Cl (wt.%)	24.12	-	21.39	14.31	8.04	5.92
K (wt.%)	-	25.02	5.30	9.21	16.32	18.44
Mn (wt.%)	-	38.17	6.10	12.41	18.77	20.13
Total (%)	100	100	100	100	100	100

The EDX analysis of the KMnO₄/AP revealed that Mn, K, Cl, O, and N elements existed in all KMnO₄/AP samples, as seen in Figure 4.4. The oxygen content remained relatively constant across samples, with ratios ranging from 20:80 to 80:20, underscoring the combined contribution of oxygen from both KMnO₄ and AP. This consistency aligns with the research's primary objective of improving the oxidiser in CSP formulations without compromising their oxidising properties. Furthermore, the mapping images of the KMnO₄/AP mixtures illustrated a uniform distribution of Cl, O, K, N, and Mn elements, with the weight percentages of each element remaining constant across the samples, as shown in Table 4.1. The data revealed a decrease in the N and Cl elements from AP with an increasing KMnO₄ to AP ratio, while the K and Mn contents from KMnO₄ increased proportionally with the ratios. These changes in elemental composition suggest that increasing the KMnO₄ weight percentage while reducing APs contributes to a more effective dual oxidiser formulation. In addition, as the KMnO₄ to AP ratio increased, the Cl element

decreased, exemplified by the Cl weight percentage in the KMnO_4/AP (20:80) sample being 21.39%, which dropped to 5.92% in the KMnO_4/AP (80:20) sample. This finding shows that incorporating KMnO_4 into AP effectively reduces the Cl element, thereby minimising the potential for HCl formation in CSP combustion by-products. In addition, the high conductivity and thermal conductivity of Mn in the KMnO_4/AP mixture will promote the formation of thermal and electrical networks throughout the system, facilitating the catalytic process of AP thermal decomposition by donating additional electrons and oxygen (Yuan et al., 2021).

4.2.4 Crystallinity Properties Analysis (XRD) of AP, KMnO_4 , and Dual Oxidiser KMnO_4/AP

The XRD patterns for ammonium perchlorate (AP), potassium permanganate (KMnO_4), and various ratios of KMnO_4/AP samples were shown in Figure 4.5, covering a 2θ range from 15° to 55° . Both AP and KMnO_4 were identified as crystallises within the orthorhombic crystal structure. Besides, this result was validated by the experiments conducted by Ismael et al. (2023) and Polis et al. (2022), confirming the appearance of AP and KMnO_4 elements associated with space groups 33 and 62, respectively. Space group means crystallography, which is the mathematical characterisation of the symmetry elements inherent in a crystal lattice, defining the dimensional repetition of the crystal (Kechit et al., 2021). For AP, a space group of 33 is described as $\text{Pna}2_1$, which is classified under the orthorhombic crystal system but contains a glide plane (n) and $a2_1$. Meanwhile, KMnO_4 , a space group of 62, characterised as

Pnma, is also classified under the orthorhombic crystal system but contains mirror planes (m) and glide planes (n and a).

Figure 4.5 reveals ten distinct peaks appeared in the AP sample (PDF Card No. 96-153-3305), which indicate the XRD pattern located at 15° , 19.3° , 24.2° , 25.1° , 27.3° , 31° , 34.7° , 41° , 48.4° , and 54.9° . These peaks correspond to the crystal planes (101), (011), (210), (102), (211), (202), (311), (203), (123), and (132), respectively. This experimental data aligns with the main peaks of AP's ASTM XRD crystallographic characteristics, as reported by (Nair et al., 2020). The arrangement of ions in the crystal structure is such that ammonium ions (NH_4^+) and perchlorate ions (ClO_4^-) are held together by ionic bonds. The ammonium ions are tetrahedrally coordinated with the perchlorate ions, forming a three-dimensional lattice, as explained by Zhang et al. (2021). In addition, the AP lattice parameter 'a' measured $9.22 \text{ \AA}$, representing the dimensions of the unit cell that makes up the crystal structure, including cell edge lengths (a, b, c) and the angles between them (α , β , γ).

For KMnO_4 plotting (PDF Card No. 96-152-1180), five peaks were observed at 15.7° , 25.2° , 25.9° , 31.2° , and 47° , corresponding to the (101), (102), (211), (301), and (303) crystal planes, respectively. These findings indicate an orthorhombic crystal structure with three unequal axes at right angles. This contrasts with the cubic or hexagonal monoclinic crystal structures, as discussed by Cai et al. (2020). The lattice parameter 'a' for KMnO_4 was determined to be $9.12 \text{ \AA}$, smaller than AP. This was attributed to the smaller size of the K^+ ion relative to the NH_4^+ ion, the distinct crystal structures and

packing efficiencies of the two compounds. The tighter packing and stronger interactions within KMnO_4 result in a more compact unit cell with smaller lattice dimensions.

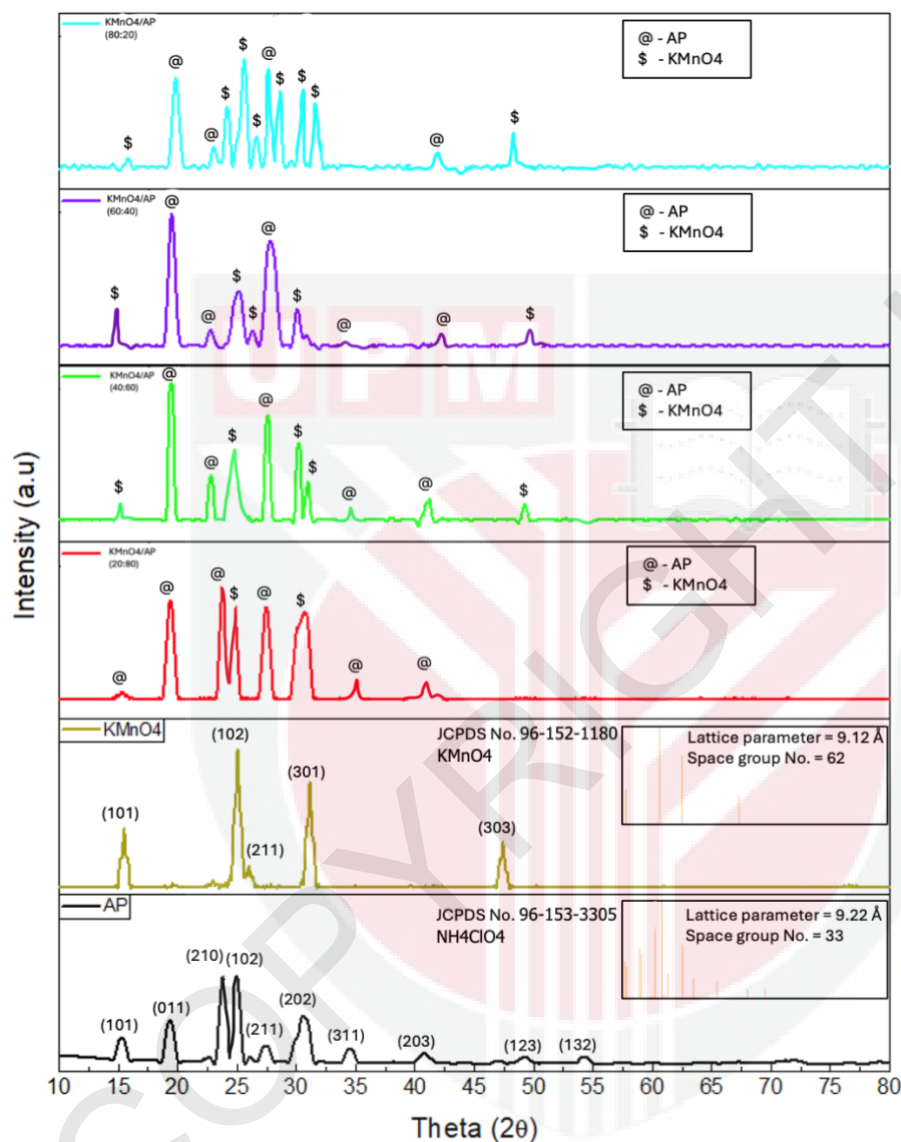


Figure 4.5: Crystallinity plot in XRD analysis of AP, KMnO_4 , KMnO_4/AP (20:80), KMnO_4/AP (40:60), KMnO_4/AP (60:40), and KMnO_4/AP (80:20)

The crystallinity plot of KMnO_4/AP samples for four different ratios consistently exhibited peaks within the 15° to 50° range. These peaks were identified using X'pert HighScore software, which allows determining specific elements and

their corresponding Miller indices (hkl) values. As the KMnO_4 to AP ratio increases, some peaks become sharper while others exhibit broadening. Additionally, the intensity of the peaks changes with the increasing ratio of KMnO_4 to AP. These variations in peak characteristics were attributed to the crystalline structures of AP and KMnO_4 . Mixing AP with KMnO_4 could result in forming a new crystalline compound or a more ordered phase for both elements. It has been observed in SEM analysis (as in subchapter 4.2.2) that some AP crystallite structures might be altered upon interaction with KMnO_4 , forming a new crystalline structure. Thus, it leads to a reduction in internal lattice strain within the crystalline material, thereby causing the formation of sharper peaks, which can be referred to as XRD peaks for sample KMnO_4/AP (40:60), KMnO_4/AP (60:40) and KMnO_4/AP (80:20) in Figure 4.5. This can be proved by the crystallite size data tabulated in Table 4.2.

Table 4.2: Crystallinity dimensions of AP, KMnO_4 , and KMnO_4/AP with different KMnO_4 to AP ratios

Sample	Peak number	Peak position (2θ)	Half the maximum intensity (β)	Crystallite size (nm)	Average Crystallite size (nm)
AP	1	15.266	0.808	9.919	11.535
	2	19.425	0.760	10.599	
	3	24.268	1.498	5.423	
	4	27.359	1.454	5.622	
	5	30.615	1.126	7.313	
	6	34.473	0.756	10.994	
	7	40.738	0.248	34.109	
	8	49.206	0.890	9.813	
	9	54.268	0.891	10.025	
KMnO_4	1	15.479	0.608	13.165	13.661
	2	25.042	0.638	12.750	
	3	31.111	0.612	13.463	
	4	47.365	0.568	15.263	

Table 4.2: (continued)

Sample	Peak number	Peak position (2 θ)	Half the maximum intensity (β)	Crystallite size (nm)	Average Crystallite size (nm)
KMnO ₄ /AP (20:80)	1	19.443	0.451	17.853	11.079
	2	23.908	0.681	11.912	
	3	24.666	0.685	11.857	
	4	27.458	0.659	12.397	
	5	30.508	1.178	6.9879	
KMnO ₄ /AP (40:60)	1	19.443	0.451	17.853	19.307
	2	22.789	0.443	18.260	
	3	23.938	0.404	20.081	
	4	24.764	0.439	18.523	
	5	27.558	0.455	17.973	
	6	30.181	0.410	20.040	
	7	30.937	0.361	22.821	
	8	34.676	0.449	18.506	
	9	41.069	0.551	15.394	
	10	49.240	0.401	21.739	
	11	54.382	0.421	21.182	
KMnO ₄ /AP (60:40)	1	15.428	0.494	25.300	21.014
	2	19.504	0.635	20.320	
	3	22.774	0.520	23.090	
	4	25.059	0.904	19.300	
	5	26.309	0.401	20.34400	
	6	27.837	0.956	25.300	
	7	30.103	0.568	19.990	
	8	34.697	0.495	16.811	
	9	42.344	0.456	18.672	
KMnO ₄ /AP (80:20)	1	19.825	0.629	20.995	22.539
	2	24.165	0.480	24.032	
	3	25.557	0.626	21.992	
	4	28.154	0.982	23.665	
	5	31.108	1.302	25.120	
	6	35.561	0.773	23.698	
	7	41.549	0.836	21.250	
	8	42.648	0.443	22.395	
	9	54.954	0.454	19.698	

Fundamentally, particle size does not correlate directly with crystalline structure. From morphology evaluation by SEM, the particle size of AP decreases, and the KMnO₄ particles become comminute due to the crushing that occurred during the synthesis process using an agate mortar. However,

due to the AP particle adhering to the KMnO_4 rod-like particle, a more significant new structure of KMnO_4/AP formed, increasing crystallinity size. This observation can be validated through the changes in the material's crystal structure and the interactions between the AP and KMnO_4 , as evidenced in the XRD peak analysis. Referring to Figure 4.5, most peaks throughout the ratios are sharper and more intense, indicating the formation of a new crystalline compound or a more ordered phase. Besides, the adhesion of AP to the KMnO_4 structure potentially reduces grain boundaries, resulting in larger or more well-defined crystallites. This reduction diminishes scattering and broadening effects, leading to the formation of sharper peaks and an increase in crystallite size. This increase in crystallite size can be proven by calculation using the Scherrer formula, as tabulated in Table 4.2. The calculation shows that the crystallite size increases with increasing ratios of KMnO_4 to AP with the values of 11.079 nm, 19.307 nm, 21.014 nm, and 22.539 nm, respectively.

4.2.5 Molecular Structure and Interaction Analysis of AP, KMnO_4 , and Dual Oxidiser KMnO_4/AP

By analysing the Raman spectra for AP, KMnO_4 , and KMnO_4/AP at varying ratios, a better understanding of molecular bonding and crystalline structure of all the samples can be achieved. Raman spectroscopy plays a crucial role in materials research and development, especially in developing novel materials that can provide insights into the structure-property relationships of materials. In this study, the spectral bands corresponding to different vibrational modes of the molecule and crystal lattice vibrations of all the samples were observed. According to Figure 4.6, all samples show a consistent trend of peaks, and it

is observed that there are some additional peaks for sample KMnO_4/AP at different ratios.

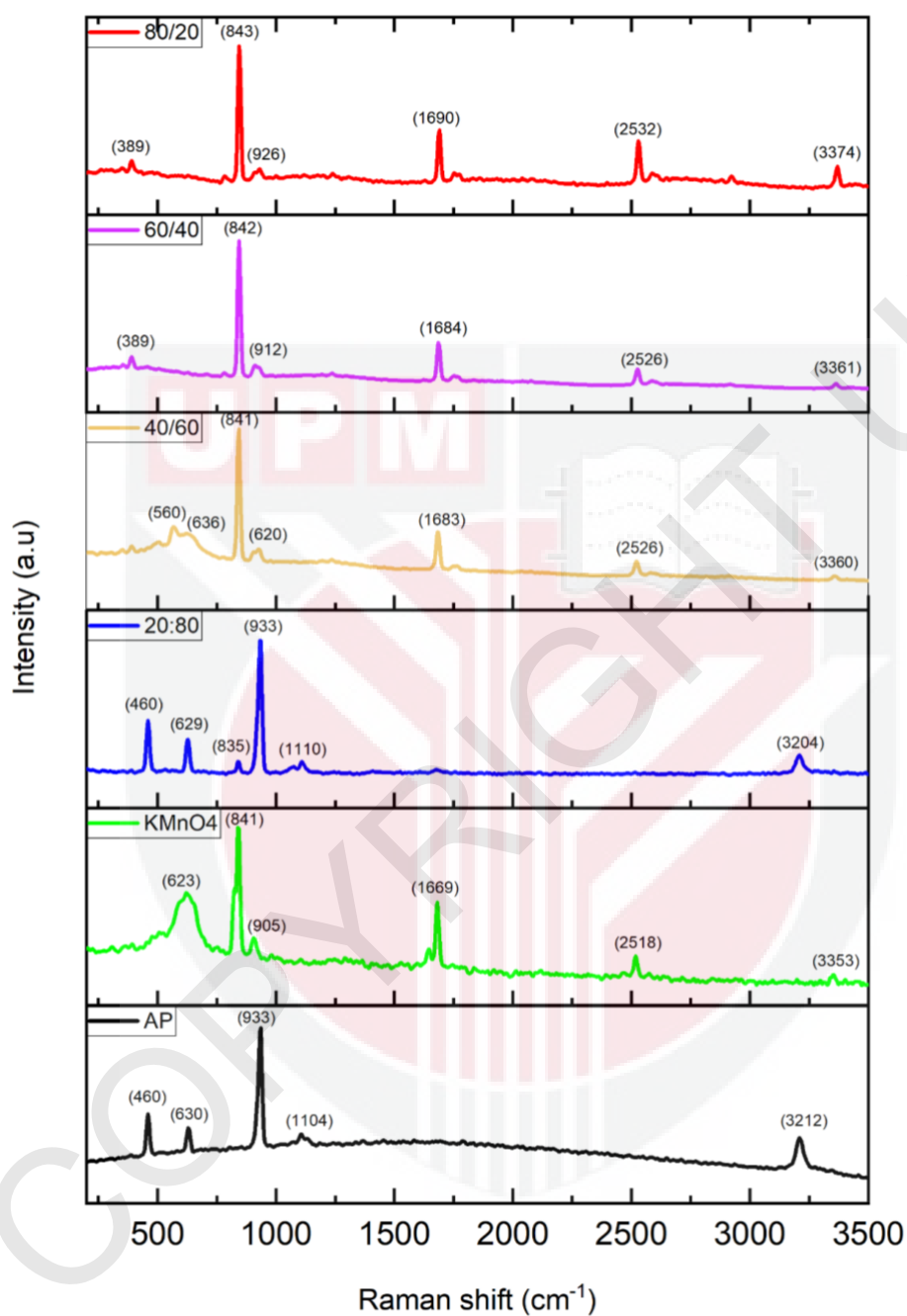


Figure 4.6: Raman spectrum of AP, KMnO_4 , and KMnO_4/AP with various KMnO_4 to AP ratios

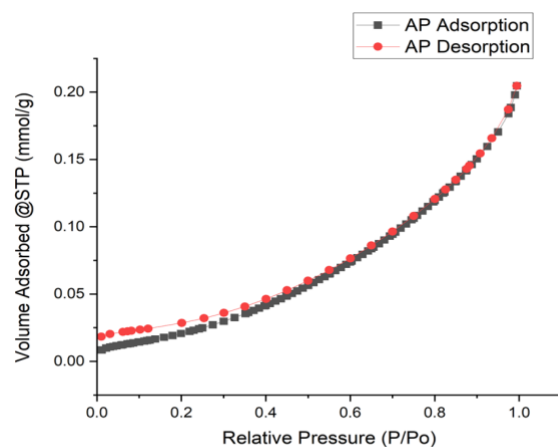
The Raman spectrum of AP reveals information about the vibrational modes associated with the motion of its constituent atoms and ions. From the AP

Raman plot presented in Figure 4.6, there are 5 distinct peaks observed corresponding to NH_4^+ symmetric and asymmetric stretching, Cl-O stretching and bending, N-H bending modes, and lattice vibrations. Similarly, the Raman spectrum of KMnO_4 exhibits 6 peaks attributed to Mn-O stretching vibrations, Mn-O bending vibrations, oxygen breathing mode, and potassium cation vibrations. In the case of the KMnO_4/AP samples at varying ratios, they exhibit a consistent curve behaviour, with a noticeable shift in the intensity of each peak to a higher frequency as the ratio of KMnO_4 to AP increases. This shift was due to increased mechanical bonding energy between KMnO_4 and AP, as discussed in section 4.2.2. This finding is aligned with an experimental data report conducted by Hess et al. (2021), in which the shifting in the Raman peak to higher intensity is because of the mechanical bonding affecting the force constants associated with the molecular or atomic vibrations of KMnO_4 to AP. Furthermore, this suggests that a higher KMnO_4 to AP ratio intensifies the interactions between KMnO_4 and AP, leading to an increased number of scattering centres, thus increasing the intensity of the Raman signal. Besides, the emergence of additional peaks with increasing ratios of KMnO_4 to AP samples was due to the formation of mechanical bonding. The newly observed peaks may indicate the formation of novel bonding interactions or structural alterations resulting from mechanical activation (Xu et al., 2008). The observation of vibrational modes in the Raman analysis supports a novel structure for KMnO_4/AP , as mentioned in sections 4.2.2 and 4.2.4, validated by adding new peaks and the peak shift to a higher intensity.

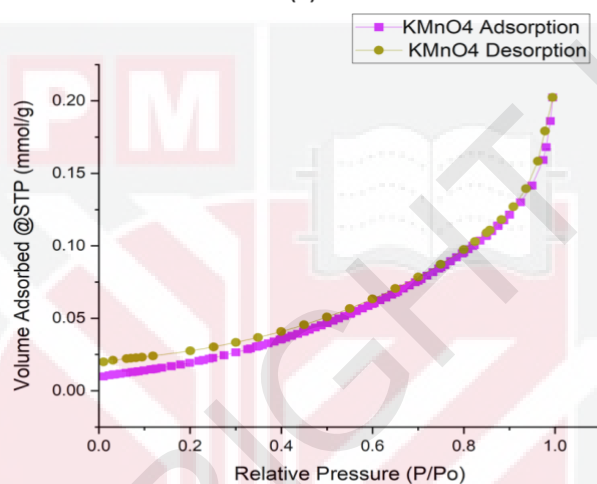
4.2.6 Surface Area Analysis of AP, KMnO_4 , and Dual Oxidiser KMnO_4/AP

The pore textural characteristics of KMnO_4/AP play a pivotal role in the thermal catalytic performance of AP, mainly due to its uniquely developed structure. This relationship has been investigated by analysing nitrogen adsorption-desorption isotherms and the pore size distributions. Figure 4.7 (a) reveals the volume of absorption and desorption of AP, while Figure 4.7 (b) shows KMnO_4 along the relative pressures. The comparison reveals minimal differences in the nitrogen absorption and desorption behaviours between AP and KMnO_4 . Furthermore, Figure 4.7 (c) illustrates the absorption and desorption plot for KMnO_4/AP samples at different ratios, highlighting that all samples exhibited a hysteresis loop, indicating the presence of mesopores.

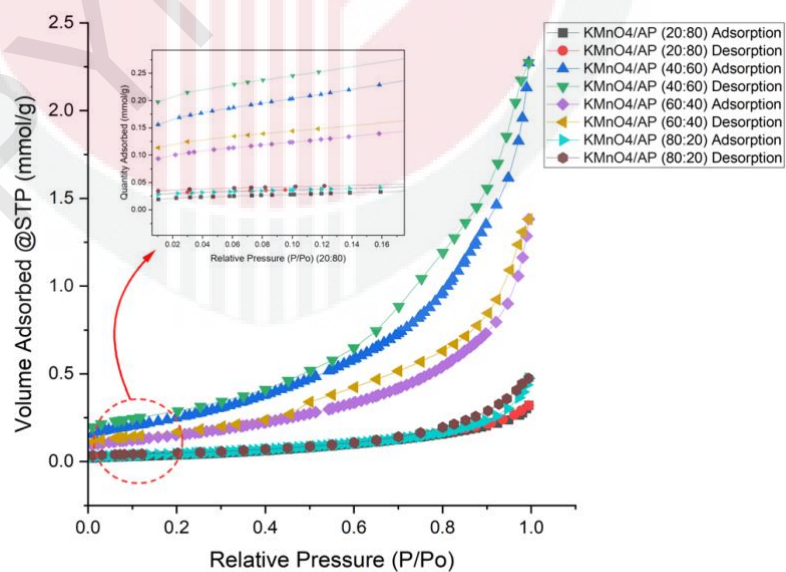
The curves presented the characteristics of I/IV mixed-type isotherms, suggesting the presence of micropores and mesopores in all samples while referring to the experimental works by Vara et al. (2019). Based on Figure 4.7 (c), it is observed that the KMnO_4/AP with a 40:60 ratio exhibits the highest adsorption and desorption volume, approximately 2.25 mmol/g, at a relative pressure of (P/P_0) of 1.0. This is followed by the KMnO_4/AP ratios of 60:40, 20:80, and 80:20, respectively. The pronounced absorption and desorption volumes indicate that this sample has a significant surface area and porosity, attributed to numerous accessible surface sites for gas molecule adsorption. These observations align with the results reported by Wang et al. (2019), which explained that a greater quantity of gas adsorbed indicates that the material possesses an increased surface area for adsorption, thus resulting in higher reactivity.



(a)



(b)

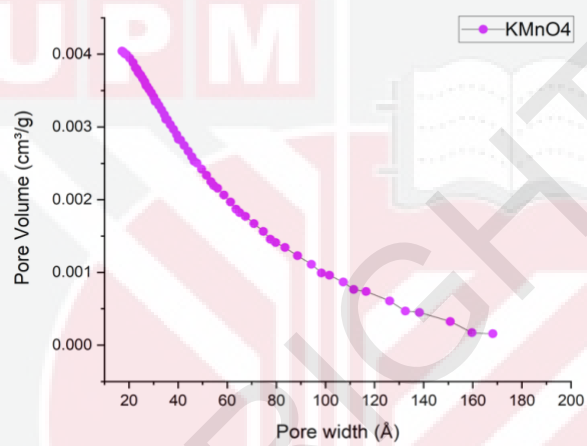
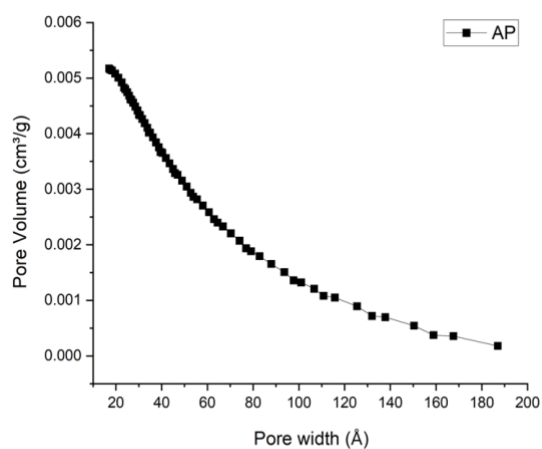


(c)

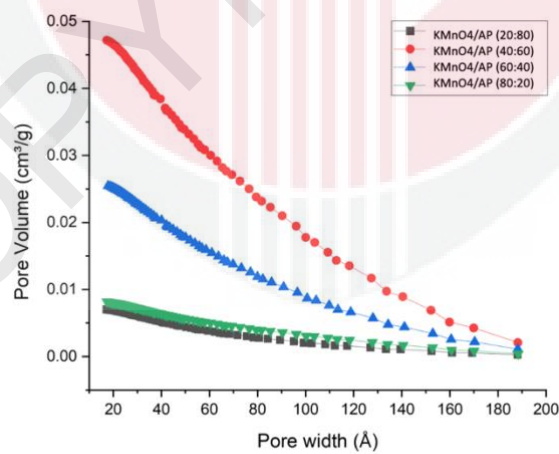
Figure 4.7: N₂ adsorption-desorption isotherms of (a) AP, (b) KMnO₄, and (c) KMnO₄/AP with different KMnO₄ to AP ratios

Besides, this higher surface area will increase active sites that are accessible for chemical reactions and enhance surface interaction among reactants. This suggests the formation of a porous structure within the KMnO_4/AP samples after the synthesis process. The pore volume versus pore width plots for the AP and KMnO_4 samples were illustrated in Figure 4.8 (a) and Figure 4.8 (b), respectively, while Figure 4.8 (c) demonstrates for all samples of KMnO_4/AP with different ratios. The specific surface area of all samples was tabulated in Table 4.3.

Figure 4.8 clearly illustrates the presence of mesopores ranging from 20 Å to 190 Å across the samples, with a less uniform distribution. With referring to Figure 4.8 (c), the KMnO_4/AP sample with a 40:60 ratio exhibits the largest pore volume, followed by the samples with ratios of 60:40, 80:20, and 20:80 with values of approximately 0.048 cm^3/g at a pore width of 20 Å. This high in pore volume implies a larger surface area available for adsorption and interaction with other substances. Besides incorporating KMnO_4 into AP, surface modification or treatments have also been made with a new KMnO_4/AP structure, which increases the surface area. For instance, the process of crushing AP particles using an agate mortar may exhibit increased surface roughness and porosity. This increased surface area can be advantageous for the KMnO_4/AP in having lower thermal decomposition temperature, thus promoting a good catalytic property that enhances CSP combustion characteristics.



(b)



(c)

Figure 4.8: Pore volume and size distributions of (a) AP, (b) KMnO₄, and (c) KMnO₄/AP with different KMnO₄ to AP ratio

In addition, a catalyst with a larger specific surface area exhibits superior catalytic activity because more electron interaction facilitates reactions (DeLuca et al., 2018). The significant specific surface area of KMnO₄/AP suggests that KMnO₄ can effectively inhibit the aggregation of AP particles, leading to a bigger agglomeration of AP particles that will reduce the specific surface area.

Table 4.3: BET surface area, pore sizes, and pore volume distribution of the AP, KMnO₄ and KMnO₄/AP with different ratios

Sample	BET (m ² /g)	Pore size (Å)
AP	2.1748	9.3934
KMnO ₄	1.9565	10.008
KMnO ₄ /AP (20:80)	6.4538	5.1520
KMnO ₄ /AP (40:60)	13.5289	2.0123
KMnO ₄ /AP (60:40)	9.8913	3.98464
KMnO ₄ /AP (80:20)	3.8660	7.7809

From the data tabulated in Table 4.3, it can be observed that the specific surface area of AP is higher than KMnO₄ with the values of 2.1748 m²/g and 1.9565 m²/g, respectively. When the ratio of KMnO₄ to AP increased, it was found that the specific surface area of the KMnO₄/AP increased from 6.4538 m²/g at a 20:80 ratio to a peak of 13.5289 m²/g at a 40:60 ratio. Beyond this point, further increases in the KMnO₄ ratio will lead to a decline in surface area, dropping to 3.8660 m²/g at a 80:20 ratio. Notably, the highest specific surface observed is at the 40:60 ratio, measuring 13.5289 m²/g. The inclusion of KMnO₄ into AP enhances the specific surface area up to the 40:60 ratio. However, beyond this ratio, adding more KMnO₄ results in a decrease in specific surface area. This might be attributed to the partial overlap between the three-dimensional structure formed by KMnO₄ and the skeletal structure

formed by KMnO_4/AP . This overlap may also impact the catalytic activity (Budhwar et al., 2018).

4.3 Catalytic Behaviour of AP, KMnO_4 , and Dual Oxidiser KMnO_4/AP

4.3.1 Thermal Decomposition Temperature of AP, KMnO_4 , and Dual Oxidiser KMnO_4/AP

Figure 4.9 displays the DSC and TGA curves depicting pure AP and KMnO_4 decomposition temperatures. Figure 4.9 (a) displays three peaks during the thermal decomposition of raw AP, which is the result achieved in an experiment conducted by Benhammada et al. (2021). The endothermic peak at 250.1 °C signifies the shift of AP to the crystalline phase. The AP transitions from an orthorhombic to a square crystal structure (Yuan et al., 2021). During the decomposition process, AP exhibits two exothermic peaks corresponding to the low-temperature decomposition (LTD) peak and the high-temperature decomposition (HTD) peak. LTD is a multiphase reaction method involving solid-gas reactions, which include decomposition and sublimation processes (Kohga et al., 2019). The LTD peak, observed at 296.4 °C, correlates with the release of gases such as chlorine dioxide (ClO_2), oxygen (O_2), and water vapour (H_2O) as reported in Dave et al. (2022). The HTD stage, occurring at 354.8 °C and primarily driven by gas-phase reactions, results in the production of gases such as nitrogen (N_2), chlorine (Cl_2), and water vapour (H_2O), releasing a significant amount of heat. This second exothermic peak, or HTD, is the most important and the highest point of the AP decomposition process, as mentioned by (Zhang et al., 2021).

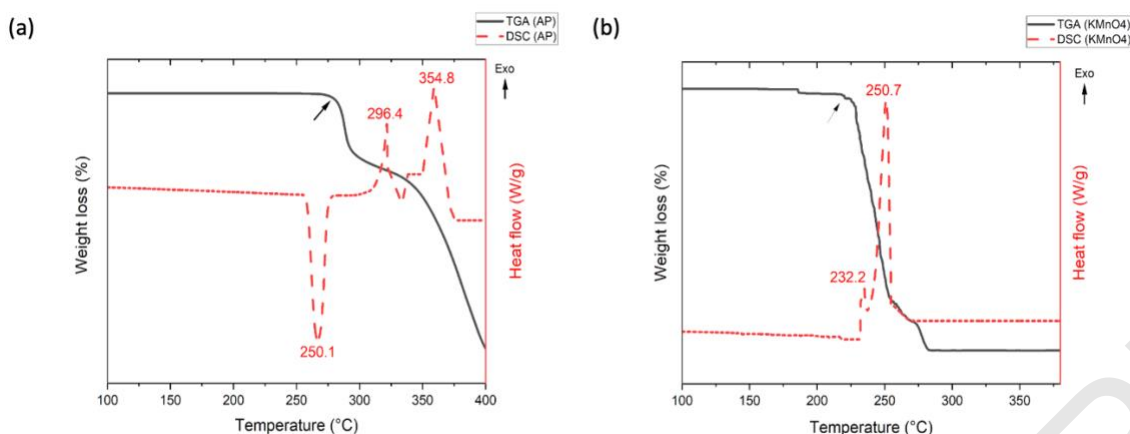


Figure 4.9: TGA and DSC result of the sample (a) AP and (b) KMnO_4

Figure 4.9 (b) illustrates the thermal decomposition behaviour of KMnO_4 . The initial weight loss at a temperature of 189.1°C was often attributed to removing adsorbed or residual moisture in the KMnO_4 sample, resulting in a slight and gradual decrease in weight (Abisha et al., 2023). As the temperature increases, KMnO_4 undergoes thermal decomposition. The most common reaction involved the breakdown of KMnO_4 into manganese dioxide (MnO_2) and oxygen gas (O_2) at a temperature of 232.2°C . This stage was characterised by significant weight loss due to the liberation of oxygen and the formation of MnO_2 (Wang et al., 2023). As the temperature continued to rise, MnO_2 decomposed into manganese (III) oxide (Mn_2O_3) until the temperature reached up to 250.7°C . The weight loss during this stage was associated with converting MnO_2 into Mn_2O_3 , as reported by Pędziwiatr et al. (2018) and Imoisili et al. (2020). Figure 4.10 illustrates the impact of various weight ratios (20:80, 40:60, 60:40, and 80:20) of KMnO_4 to AP on the AP thermal decomposition temperature through (a) TGA and (b) DSC analysis.

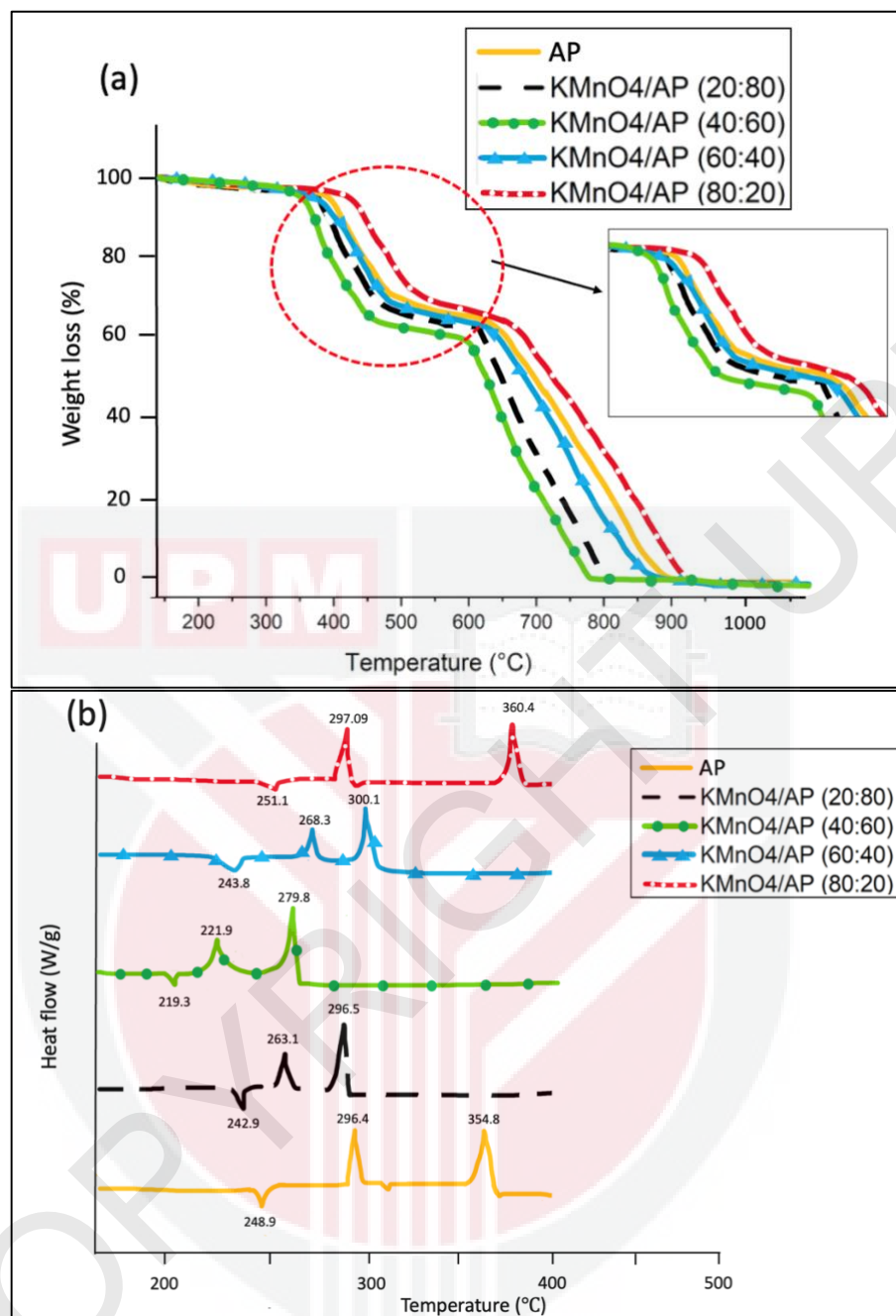


Figure 4.10: Analysis result of (a) TGA and (b) DSC of KMnO₄/AP samples with different ratios

Figure 4.10 (a) displays the weight loss progression for the AP and KMnO₄/AP samples with ratios 20:80, 40:60, 60:40, and 80:20, exhibiting a typical and consistent trend throughout the temperature range. The curves reveal that for all ratios, the KMnO₄/AP samples exhibited two peaks, indicative of two

exothermic reactions during the decomposition process, which was similar to the AP thermal decomposition behaviour prior to complete decomposition. Besides, the KMnO_4/AP samples with ratios of 40:60, 20:80, and 60:40 demonstrated an earlier onset of decomposition temperature at both LTD and HTD peaks compared to pure AP, with the 40:60 ratio showing the earliest decomposition. However, the KMnO_4 with 80:20 ratio resulted in higher thermal decomposition temperature at both peaks than AP. This indicates that incorporating KMnO_4 with AP enables the sample to undergo decomposition at low temperatures to complete the entire combustion process. Sangtyani et al. (2019) reported that lower decomposition temperatures can lead to higher burn rates at lower temperatures, which is beneficial for enhancing the efficiency and performance of the propulsion systems by generating thrust without excessive heating. This finding shows that KMnO_4 acts as a catalyst in the AP decomposition process by reducing the thermal decomposition temperature of AP without compromising the behaviour until the complete combustion (weight loss is 0%). In addition, this data reported is consistent with the exothermic peaks shown in the DSC curves illustrated in Figure 4.10 (b).

From Figure 4.10 (b), the DSC curve was plotted, showing that all samples followed the typical AP characteristics trend with one endothermic and two exothermic peaks, as reported by Wang et al. (2018). Based on the curve in Figure 4.10 (b), the incorporation of KMnO_4 slightly reduced the endothermic decomposition temperature peak of AP at ratios of 20:80, 40:60, and 60:40, at a ratio of 80:20, the temperature was observed to increase slightly. For

example, the KMnO_4/AP sample with a 40:60 ratio decreased the AP decomposition temperature at the endothermic reaction peak from 248.9°C to 219.3°C , nearly doubling the effect. This DSC curve clearly illustrated the reduction in LTD and HTD of AP from the TGA curve, specifying the temperature values for each peak. For example, the LTD of AP for the KMnO_4/AP samples with ratios of 20:80, 40:60, and 60:40 shifted from 296.4°C to 263.1°C , 221.9°C , and 268.3°C , respectively. Besides, the HTD of AP was reduced from 354.8°C to 296.5°C , 279.8°C , and 300.1°C for the KMnO_4/AP samples at ratios of 20:80, 40:60, and 60:40, respectively. Conversely, the KMnO_4/AP sample with a ratio of 80:20 shows the opposite behaviour from the other KMnO_4/AP samples, resulting in an increase in the endothermic decomposition temperature, LTD and HTD of AP with values of 251.1°C , 297.09°C , and 360.4°C , respectively. Based on these temperature values, the KMnO_4/AP sample with a ratio of 40:60 exhibited the most catalytic effect, as it shifted the LTD and HTD of AP to the lowest decomposition temperature values compared to others.

Besides, as the ratio of KMnO_4 to AP increases, the HTD peak tends to disappear and merge with the LTD. The consumption of AP and KMnO_4 in HTD reactions means that AP could be depleted together with KMnO_4 , potentially diminishing the reaction rate or the occurrence of HTD. It also has been observed that among the samples, the exothermic peaks of KMnO_4/AP (40:60) were the most pronounced in terms of heat flow value, indicating that this particular sample exhibits the highest heat release during the combustion process. Specifically, the KMnO_4/AP (40:60) sample achieved the highest heat

release (ΔH) throughout the temperature range, with values reaching 1759.5 J/g. The catalytic activities of the samples examined in this study were summarised in Table 4.4.

Table 4.4: Low-temperature decomposition (LTD), high-temperature decomposition (HTD) and heat release (ΔH) results of all the samples in this study

Sample	LTD(°C)	HTD(°C)	ΔH (J/g)
AP (pure)	296.4	354.8	552.4
KMnO ₄ /AP (20:80)	263.1	296.5	1503.8
KMnO ₄ /AP (40:60)	221.9	279.8	1759.5
KMnO ₄ /AP (60:40)	268.3	300.1	1090.2
KMnO ₄ /AP (80:20)	297.09	360.4	529.1

To further illustrate the distinct impacts of KMnO₄/AP, a comparative analysis was conducted to assess their catalytic activities in relation to the LTD and HTD peaks, as well as the heat release compared with alternative catalysts reported in the literature for AP thermal decomposition. According to the finding presented by Zhao et al. (2016), incorporating carbon nanomaterials and copper offers advantages in enhancing the thermal decomposition efficiency of AP. However, the addition of KMnO₄ to AP composites, even compared to those comprising solely of copper or carbon nanomaterials, led to a more significant advancement of both LTD and HTD peaks of AP. Table 4.5 shows a comparison of LTD, HTD and heat release from the literature with samples in this research. Furthermore, it is evident from Table 4.5 that the released heat (ΔH) by KMnO₄/AP (40:60), a crucial parameter in the thermal decomposition of AP, is higher than that of most catalysts reported.

Table 4.5: Thermal decomposition performance of AP in this work compared with the literature

Sample	LTD (°C)	HTD (°C)	ΔH (J/g)	References
KMnO ₄ /AP (40:60)	221.9	279.8	1759.5	Current research work
CuO NPs +AP	317.0	359.0	1360.0	Wang et al., 2019
Fe ₂ O ₃ + AP	240.	367.2	N/A	Liu et al., 2012; Zhang et al., 2021
Fe ₂ O ₃ /CNT + AP	241.1	329.4	N/A	Liu et al., 2012
rGoFe ₂ O ₃ + AP	321.2	361.3	N/A	Zhang et al., 2021
3D-(N)GFs + AP	364.0	415.0	890.0	Hosseini et al., 2018
(3,5-DNB) ₂ FeCu + AP	306.0	348.6	786.0	Zhao et al., 2016
Mn@3D-(N)GFs + AP	310.6	327.8	1629.8	Jianxun et al., 2007; Hosseini et al., 2018
Ni@3D-(N)GFs + AP	307.1	414.4	1282.8	Hosseini et al., 2018
CNTs + AP	370.4	422.4	1372.0	Zhao et al., 2016
Cu/CNTs + AP	352.6	341.2	1148.0	Benhammada et al., 2021
CuO + AP	282.8	316.8	1344.9	Wang et al., 2019

4.4 Characterization of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO₄/AP) Based

4.4.1 Physical Characteristics of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO₄/AP) Based

The CSP samples were fabricated according to the previously mentioned method, and some differences were observed after curing. Figure 4.11 illustrates the samples' physical condition following the curing process.

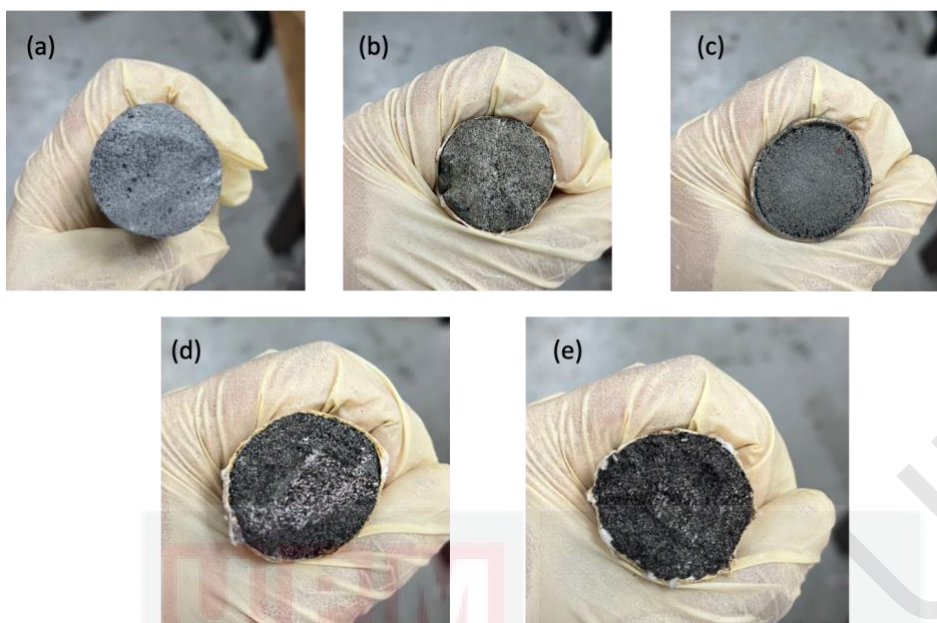


Figure 4.11: Physical condition of (a) AP CSP, (b) KMnO_4/AP (20:80) CSP, (c) KMnO_4/AP (40:60) CSP, (d) KMnO_4/AP (60:40) CSP, and (e) KMnO_4/AP (80:20) CSP

As in Figure 4.11 (a), the AP CSP sample exhibited a typical CSP colour, appearing grey with white particles dispersed throughout. This grey colour originated from the aluminium particles, while the small white particles were AP. In the presence of KMnO_4 , the CSP samples darkened, and their surfaces became rougher, as seen in Figure 4.11 (b). As the KMnO_4 to AP ratio increased, the samples progressively darkened. At ratios of 60:40 and 80:20, KMnO_4 particles became visible on the sample surfaces, as illustrated in Figures 4.11 (c) and 4.11 (d), respectively. This darkening is attributed to the incorporation of KMnO_4/AP as a dual oxidiser, with their composition being dominant. Furthermore, the uniform appearance of the dark colour indicated that the KMnO_4/AP was homogeneously mixed within the CSP systems across all samples. In an experimental work done by Yan et al. (2018), they observed

that the physical condition of the cured propellant containing iron oxide was dull, and there was an increase in surface roughness.

4.4.2 Morphological Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO₄/AP) Based

The oxidiser, specifically AP, was an organic crystal characterised by a primarily elastic response, in contrast to the elastomeric binder. This binder, a rubbery substance such as polybutadiene-acrylonitrile-acrylic acid (PBAN) or hydroxy-terminated polybutadiene (HTPB), acts as a cushion for the oxidiser. The fuel, like metallic powdered aluminium, exhibited an elastoplastic behaviour. Determining the total constitutive response of a composite material under load presents significant challenges, as it requires bridging the deformation of the component phases across two completely distinct regimes: viscous and elastic (de Francqueville et al., 2021). The evolution of the microstructure, notably as larger oxidiser particles debonded from the matrix, a process known as dewetting (Kashif et al., 2021), during straining and the formation of interfacial microcracks or holes. The material's high nonlinear macroscopic reaction could be attributed to this microstructural degradation.

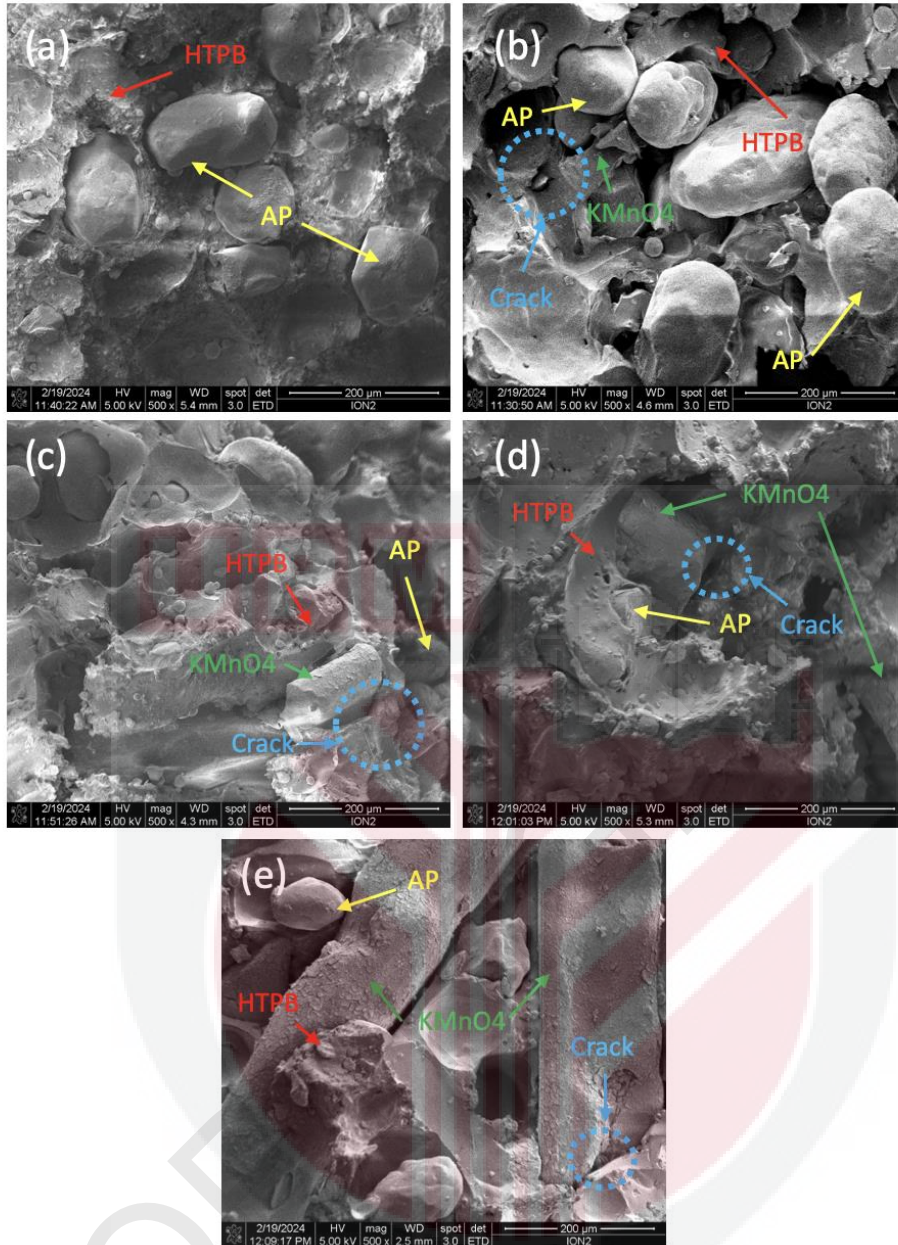


Figure 4.12: SEM image of composite solid propellant samples of (a) AP, (b) KMnO_4/AP (20:80), (c) KMnO_4/AP (40:60), (d) KMnO_4/AP (60:40), and (e) KMnO_4/AP (80:20) based

In this experimental work, images were taken with 200X magnification to examine the morphological structure of the propellant samples. Based on Figure 4.12, all samples showed typical characteristics of AP-based CSP, with proper blending of binder and oxidiser observed. These morphological

structure results were consistent with experimental data presented by Kosiba et al. (2017). Based on Figure 4.12 (a), the white spherical particles visible on the surface were identified as oxidiser particles, which were surrounded by a polymer binder, HTPB. This polymer binder was observed as a rubbery matrix structure that holds and interacts with AP particles. Examining this interface facilitated the evaluation of binder-AP adhesion, interfacial interactions, and the presence of any interfacial layers or phases (Bihari et al., 2021). Besides, a strong and uniform binder-AP interface is essential for efficient energy transfer during combustion. In Figure 4.12 (b), the rubbery structure was observed on the propellant's surface, especially on the boundary between KMnO_4/AP . The HTPB may impart a certain degree of flexibility. However, the binder primarily holds the solid KMnO_4/AP particles, leading to a brittle condition in the structure. This can be clearly seen by the formation of cracks on the boundary between KMnO_4/AP , as represented in the blue circle. This can be attributed to the incorporation of 20% of KMnO_4 , which is a rod-like solid structure interposed between AP particles and the HTPB matrix.

As the ratio of KMnO_4 increased, the rod structure of KMnO_4 became clearly visible, as in Figure 4.12 (c). For this KMnO_4/AP with a 40:60 ratio, it clearly can be seen that it exhibits a smoother surface compared to sample KMnO_4/AP (20:80). The smooth patches may signify places where a binder envelops the oxidiser particles. In contrast, the rough or jagged parts could denote the exposed surfaces of crystalline KMnO_4 and AP. In addition, it was observed that the size of AP particles decreased from approximately 100 μm to 50 μm , and the structure of KMnO_4 also became shorter. Moreover, the

reduction in AP size made it more difficult to observe the particles as they became smaller and their shape more flattened compared to their original spherical form. The KMnO_4/AP (60:40) sample seems to have the same morphological structure as the KMnO_4/AP (40:60) sample, as it results in a more compact structure, as in Figure 4.12 (d). This compactness will lead to a higher burning efficiency as the pores in the CSP surface structure can affect the combustion performances. Increasing the KMnO_4 to AP ratio made the KMnO_4 structure more visible, and the AP particles seemed to disappear. In this sample, KMnO_4 is dominant in the system, making the HTPB matrix system more ductile as it holds more KMnO_4/AP . This can introduce the formation of voids, as seen in Figure 4.12 (e), at the boundary between solid particles and the HTPB matrix. Kou et al. (2024) reported that these gaps or voids at the interfaces could reduce the material's thermal properties and burn rate performance.

4.4.3 Elemental Composition Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO_4/AP) Based

EDX mapping enabled the visualisation of elemental distribution within the microstructure of the propellant sample. By acquiring X-ray spectra at multiple points across the sample surface, EDX mapping generates elemental maps highlighting the spatial distribution of different elements. This facilitated the identification of compositional gradients, phase segregation, or localised enrichment of some aspects within the propellant. Figure 4.13 shows the EDX mapping results and the graph elemental composition intensity for the entire microstructure surface of each sample. The primary elements present in the

AP-based CSP were carbon (C), oxygen (O), nitrogen (N), aluminium (Al), hydrogen (H) and chlorine (Cl). The elements O, N, H, and Cl originated from AP, as discussed previously, while C and Al were contributed by HTPB and aluminium powder, respectively. The weight percentages of all the chemical compositions were analysed and tabulated in Table 4.6. Elemental analysis indicated no interfering elements were identified in the microscale AP's chemical structure.

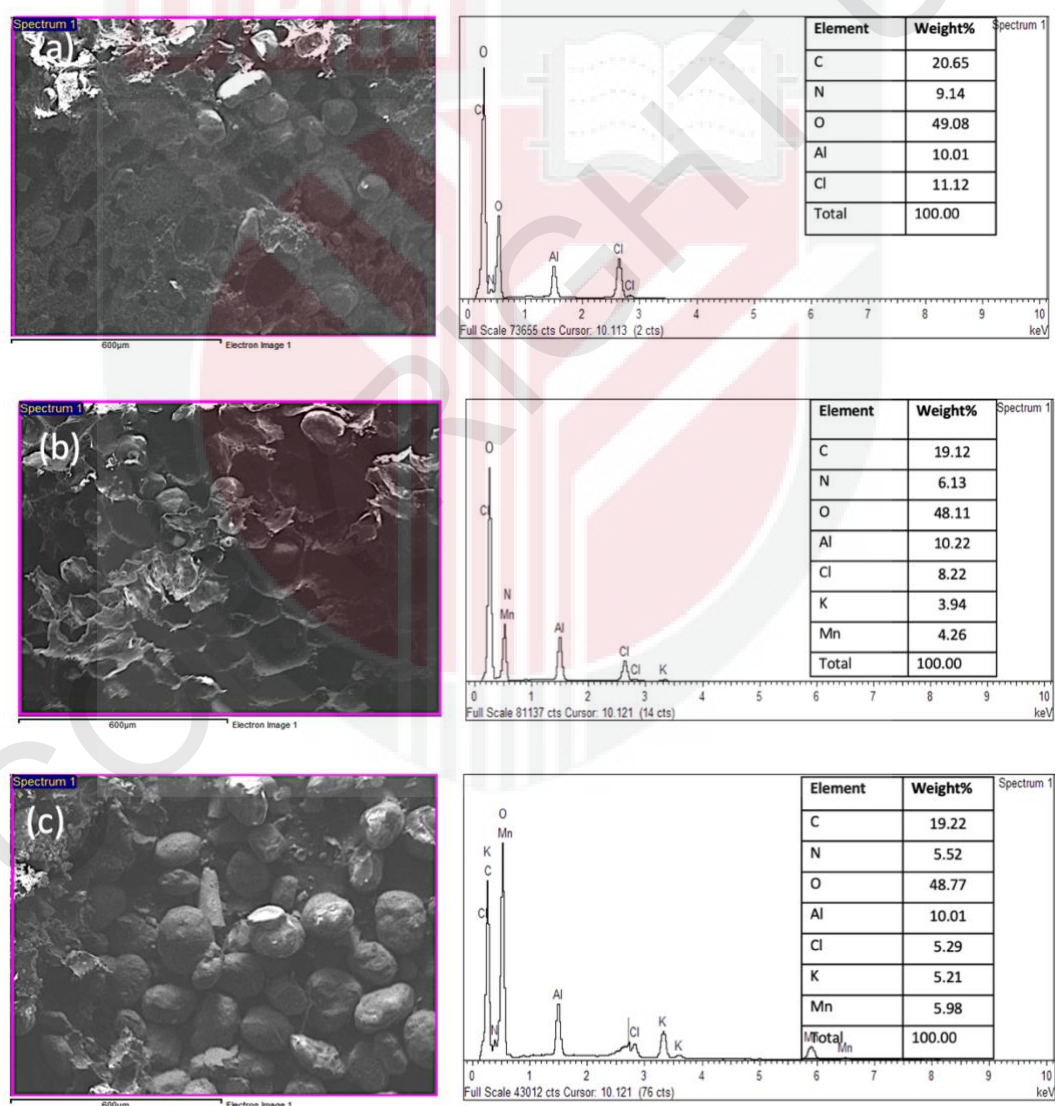


Figure 4.13: EDX mapping of (a) AP-based CSP (b) KMnO₄/AP (20:80) based CSP (c) KMnO₄/AP (40:60) based CSP (d) KMnO₄/AP (60:40) based CSP, and (e) KMnO₄/AP (80:20) based composite solid propellant

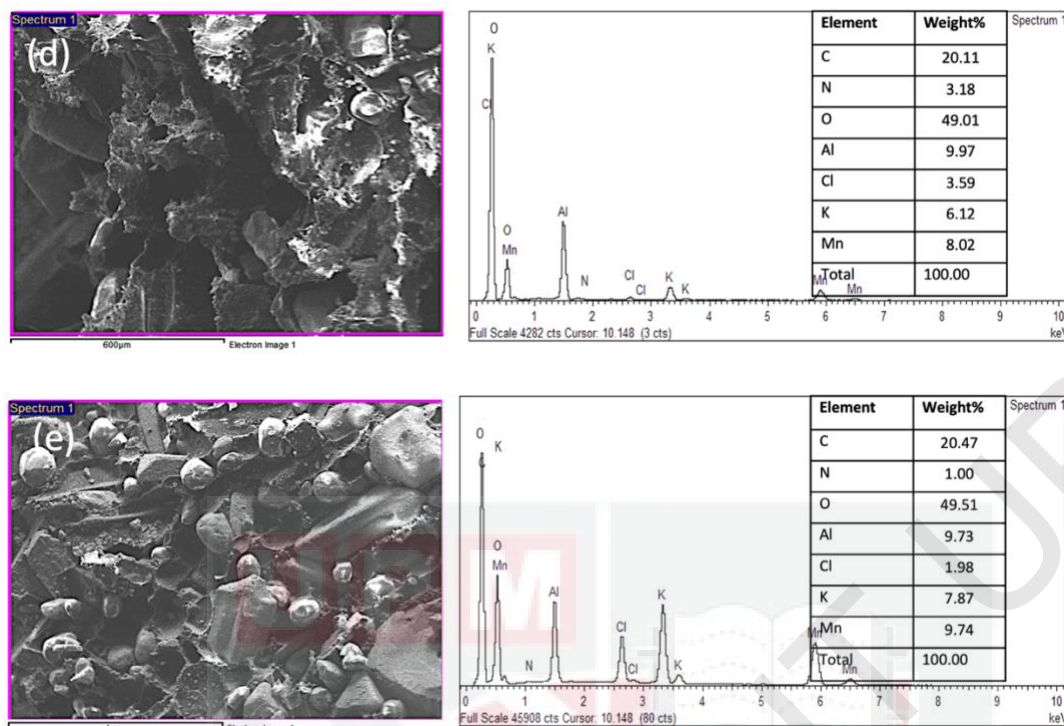


Figure 4.13: (continued)

The EDX results for all CSP samples, as illustrated in Table 4.6, showed that the oxygen weight percentage remained constant across the samples as the ratio of KMnO_4 to AP increased. The detected O element ranged from 19.5% to 20%, indicating no significant changes in the oxygen content with the increased ratio of KMnO_4 to AP. Besides, incorporating KMnO_4 into the AP-based CSP system resulted in the detection of additional elements, potassium (K) and manganese (Mn), which originate from KMnO_4 . This detection confirms that KMnO_4 was well integrated into the AP-based CSP system, as previously discussed in the morphology analysis via SEM. Notably, the weight percentage values of the K and Mn elements increased as the KMnO_4 to AP ratio was raised. This increase is qualitatively observable from the CSP sample colour changes, which became progressively darker, and the purple colour became more intense as the KMnO_4 to AP ratio increased.

Furthermore, a decrease in the Cl element's weight percentage value was observed with an increasing ratio of KMnO_4 to AP. This can be seen in AP-based CSP; the Cl element's composition weight percentage was 11.12%. However, when KMnO_4 was added in ratios of 20:80, 40:60, 60:40, and 80:20, the Cl element composition decreased to 8.22%, 5.29%, 3.59%, and 1.98%, respectively. This notable finding is attributed to the minimum use of AP, from which the Cl element exclusively originates. According to Trache et al. (2017), using Cl in the propellant composition should result in lower production of HCl gases as a combustion by-product, thereby achieving the research goal of minimising HCl as toxic gas from the combustion product of AP-based CSP systems. Furthermore, as mentioned in the previous subchapter, the hydrogen (H) element could not be detected in EDX analysis due to the low atomic number. However, it still exists and contributes through the binder and curing agent.

Table 4.6: EDX result analysis of CSP with single oxidiser AP and dual oxidiser KMnO_4 /AP

Composite solid propellant sample	Element	Weight percentage (wt.%)
AP	C	20.65
	N	9.14
	O	49.08
	Al	10.01
	Cl	11.12
KMnO_4 /AP (20:80)	C	19.12
	N	6.13
	O	48.11
	Al	10.22
	Cl	8.22
	K	3.94
	Mn	4.26

Table 4.6: (Continue)

Composite solid propellant sample	Element	Weight percentage (wt.%)
KMnO ₄ /AP (40:60)	C	19.22
	N	5.52
	O	48.77
	Al	10.01
	Cl	5.29
	K	5.21
	Mn	5.98
KMnO ₄ /AP (60:40)	C	20.11
	N	3.18
	O	49.01
	Al	9.97
	Cl	3.59
	K	6.12
	Mn	8.02
KMnO ₄ /AP (80:20)	C	20.47
	N	1.00
	O	49.51
	Al	9.73
	Cl	1.98
	K	7.87
	Mn	9.74
Total		100

This analysis also revealed a uniform distribution and well-distributed scattering of all elements across the samples, as the weight percentages of all the elements in every sample yielded uniform values. Similarly, experimental work by Sharma et al. (2015) developed Copper oxide (CuO) through green synthesis as catalytic materials for AP CSP, achieving comparable results.

4.4.4 Thermal Decomposition Analysis of Composite Solid Propellant (CSP) With Dual Oxidiser (KMnO₄/AP) Based

The thermal decomposition behaviour of AP-based CSP was investigated and compared with KMnO₄/AP-based formulations at various ratios. Figure 4.15 shows the TGA and DSC graphs for the AP-based CSP samples from the

experimental work. The TGA curve showed three stages of thermal decomposition at temperatures ranging from 100 °C to 1000 °C. The propellant sample experienced different reactions at each stage, resulting in distinct endothermic and exothermic peaks on the DSC curve. The pattern of mass loss pattern in the first and second stages (Stage I and II, respectively) showed the common thermal reaction of the AP-based CSP aligning with the experimental data from Fertassi et al. (2023). Based on Figure 4.14, Stage I was characterised by a rapid phase of mass loss at low temperatures, occurring between 100 °C and approximately 430 °C, where 80.5% of the mass was lost.

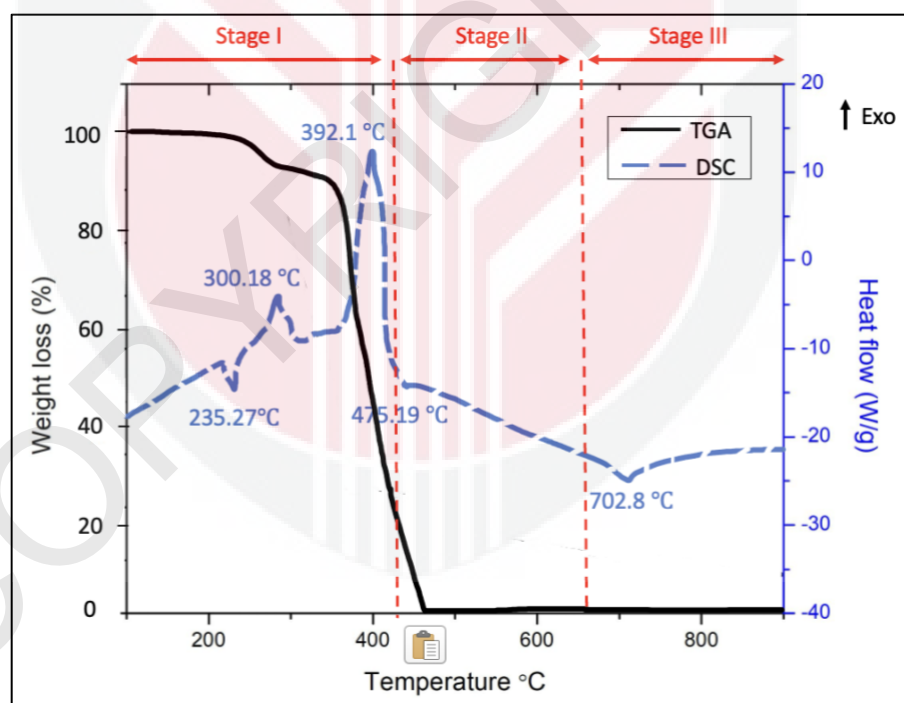


Figure 4.14: TGA and DSC result of samples AP-based CSP

AP played a significant role in influencing the overall thermal decomposition properties of the sample as the primary propellant component and oxidiser.

The transition of AP from an orthorhombic to a cubic crystalline phase was characterised by an endothermic peak at 235.27 °C, initiating the early mass loss primarily due to the evaporation or decomposition of performance modifiers like plasticisers, as explained by Zhou et al. (2020). The onset of AP's partial decomposition and the creation of intermediates were indicated by the comparatively modest exothermic peak around 300.18°C. Further decomposition of all remaining AP and the intermediates primarily contributed to the exothermic peak observed at the higher temperature of 392.1 °C. Prior research by Zhou et al. (2020) stated that HTPB underwent depolymerisation, cyclisation, and cross-linking in this stage. According to Wang et al. (2022), the most significant exothermic peak on the DSC curve was located at 392.1 °C, suggesting a rapid acceleration in the thermal decomposition of both AP and HTPB at this stage. The relatively high temperature caused the decomposition rates of HTPB and AP to accelerate, releasing copious amounts of heat and producing various oxidising gases. The oxidising gases accelerated the thermal breakdown of AP and HTPB by reacting with it and releasing additional heat.

Stage II represented a period of gradual mass loss within the medium temperature range of 420°C to 650°C. The exothermic peak observed between 440°C and 500°C, alongside a minor mass loss step on the TGA curve, was attributed to the decomposition of residual HTPB. Additionally, a moderate exothermic peak within this temperature range resulted from the oxidation of Al particles, which were gradually exposed from the HTPB matrix during this stage (Emelyanov et al., 2020). The third phase, identified as Step

III, was characterised by a slow mass gain at high temperatures. At this point, the TGA/DSC curve represented the oxidation of Al particles, with the endothermic peak appearing around 702.8°C, indicating the melting point of Al. The TGA results for the AP CSP sample were compared with those of a KMnO_4/AP -based CSP, utilising a different KMnO_4 to AP ratio, as shown in Figure 4.15. This comparison was conducted to examine the impact of the KMnO_4 to AP ratio on the endothermic and exothermic peaks of the AP CSP decomposition properties.

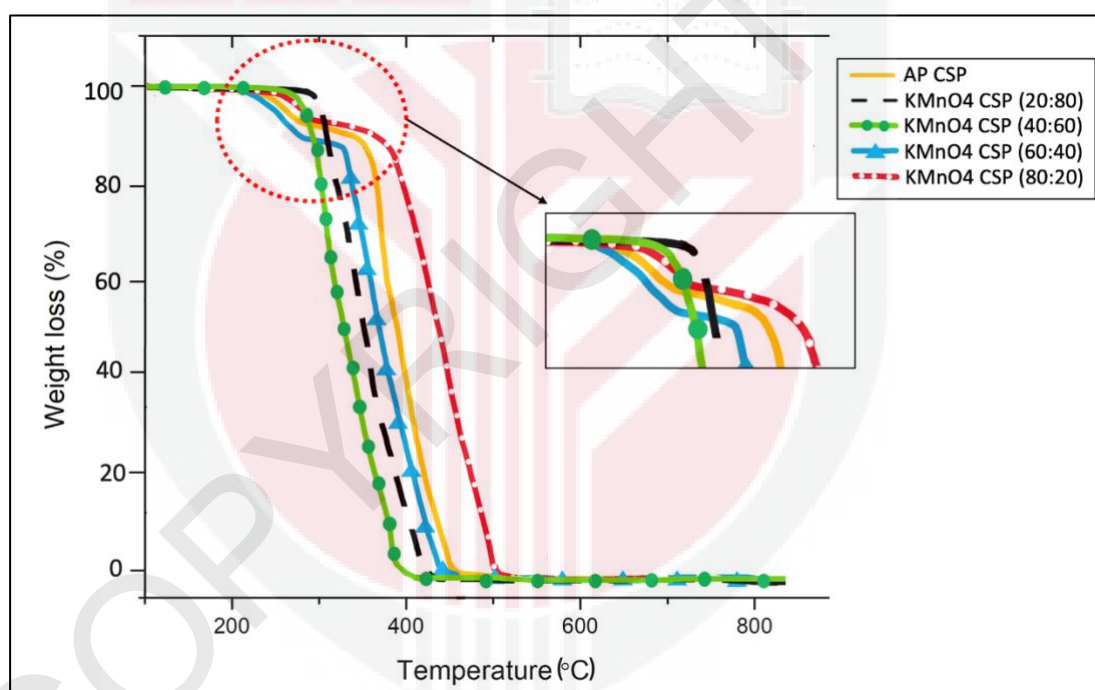


Figure 4.15: TGA plotting results of samples AP and KMnO_4/AP with different ratios based on CSP

Based on Figure 4.15, all samples resulted in similar weight loss percentage behaviours to the AP-based CSP sample, except the KMnO_4/AP CSP (20:80) and KMnO_4/AP CSP (40:60) samples. Specifically, the KMnO_4/AP CSP (20:80) and KMnO_4/AP CSP (40:60) samples exhibited only one significant

weight loss point or peak at onset temperature. In contrast, the other samples followed the typical TGA behaviour of AP composite, displaying two weight loss points. This phenomenon of different numbers of weight loss points represents that there is only one exothermic peak in sample KMnO_4/AP CSP (20:80) and sample KMnO_4/AP CSP (40:60) compared to other samples in the overall thermal decomposition process. The illustration of this result can be observed and evaluated on each of the curves through the DSC plot in Figure 4.16. In addition, it can be seen that the onset temperature of both KMnO_4/AP CSP (20:80) and KMnO_4/AP CSP (40:60) samples occurred at the earlier temperature of the significant weight loss point, but later temperature of the onset temperature compared to other samples with value of 331.32°C and 352.34°C respectively. KMnO_4/AP CSP (40:60) sample exhibits an onset temperature at the lower temperature compared to KMnO_4/AP CSP (20:80), which indicates that the thermal decomposition occurred at the lower temperature. This point (initial weight loss point) is continuously decreased until the weight loss of the sample is 100%. During this time, the decomposition process of all the compositions in the sample is completed. Besides, KMnO_4/AP CSP (60:40) and KMnO_4/AP CSP (80:20) samples resulted in two distinct weight loss points as AP CSP sample which the sample KMnO_4/AP CSP (60:40) occurred at the lower temperature followed by AP CSP and KMnO_4/AP CSP (80:20) sample at each weight loss point. The shifting of this weight loss temperature point to a lower temperature indicates that with the addition of KMnO_4 in the AP CSP system with KMnO_4 to AP ratio of 20:80, 40:60, 60:80, the thermal decomposition of the composition in the system took place at the low temperature. Adding KMnO_4 until 80% ratio to AP resulted in

the opposite performance as this sample resulted in higher weight loss temperature at all points. However, the KMnO_4/AP (80:20) sample is thermally more stable, meaning it can withstand higher temperatures without breaking down prematurely compared to others.

According to Dong et al. (2022), the lower weight loss temperature in catalysed AP solid propellant is due to the catalyst's role in lowering the activation energy, enhancing the reaction kinetics, and facilitating the thermal decomposition rate, which improves the overall efficiency of the propellant. In this research work, the KMnO_4 acts as a catalyst in the combustion process of the AP CSP system by lowering the thermal decomposition temperature to a lower temperature. This experiment's result on reducing the onset decomposition temperature is similar to experimental works conducted by Yang et al. (2024) in which incorporating highly catalytic active $\alpha\text{-Fe}_2\text{O}_3$ in AP/HTPB-based CSP system will lower the onset decomposition temperature and result in only one weight loss point.

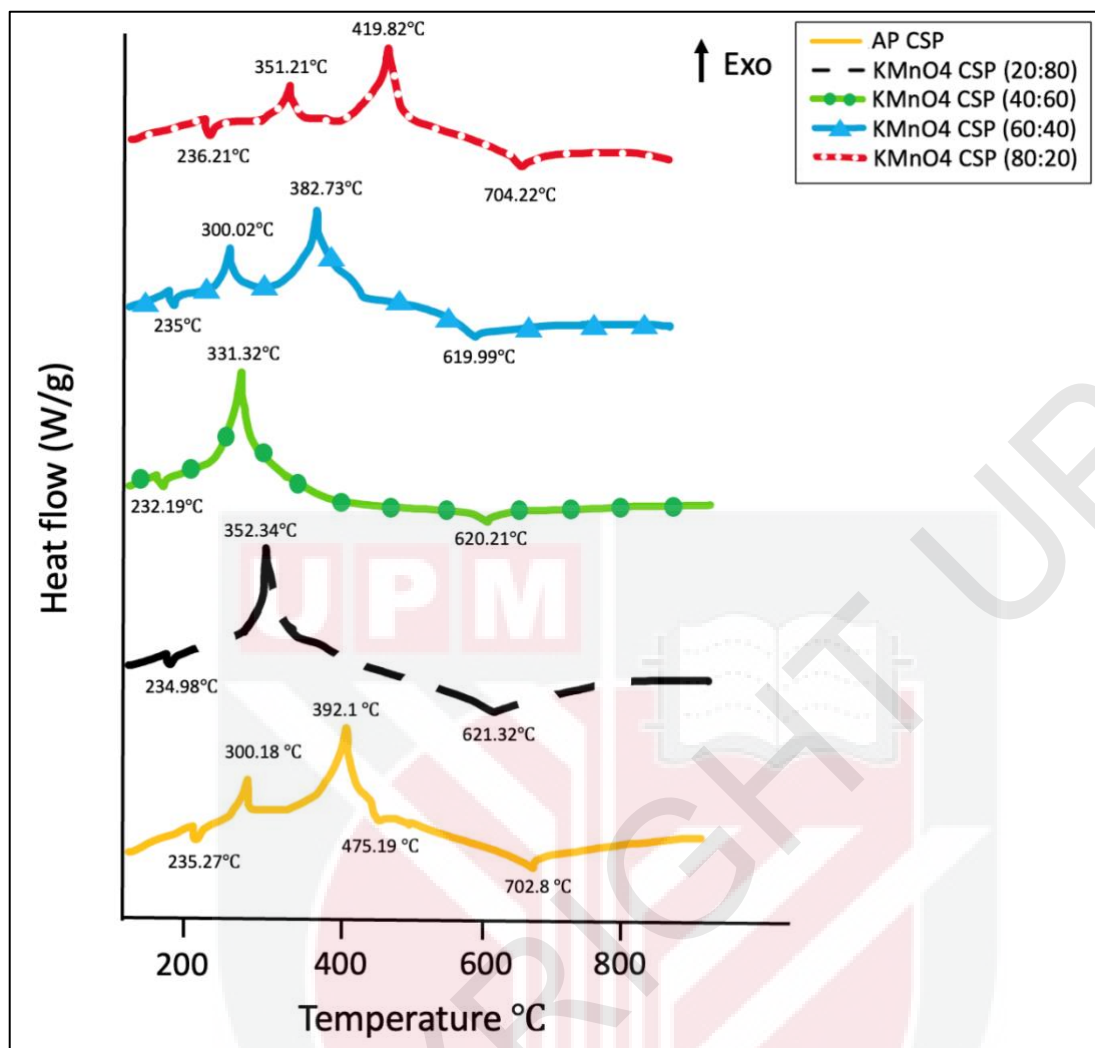


Figure 4.16: DSC plotting results of samples AP and KMnO₄/AP with different ratios based on CSP

Figure 4.16 illustrates the DSC plot for all samples, revealing that the KMnO₄/AP CSP (60:40) and (80:20) samples exhibited similar behaviour as the AP CSP. However, the KMnO₄/AP CSP (20:80) and KMnO₄/AP CSP (40:60) samples showed a different trend, similar to the TGA curve previously discussed. The KMnO₄/AP CSP samples with a ratio of 60:40 and 80:20 demonstrated show the same pattern as the AP CSP, displaying an initial endothermic peak followed by two exothermic peaks ending with one endothermic peak representing the aluminium melting phase. Meanwhile, the

KMnO₄/AP CSP (20:80) and KMnO₄/AP CSP (40:60) samples resulted in one initial endothermic peak and a single main exothermic peak, ending with one aluminium endothermic peak during the melting phase. No significant changes were observed in the first endothermic peak across all samples, but the second exothermic peak varied considerably, whereas the first exothermic peak showed minimal variation. It was observed that the two exothermic peaks, specifically the low-temperature decomposition (LTD) and high-temperature decomposition (HTD) occurring in the temperature range of 300°C to 410°C merged into a single exothermic peak in both the KMnO₄/AP CSP (20:80) and KMnO₄/AP CSP (40:60) samples. This merging may be attributed to the catalytic effect of KMnO₄, causing the reactions corresponding with LTD and HTD to overlap or occur simultaneously. Besides, as presented in section 4.3.2, the existence of KMnO₄ as a catalyst in the decomposition of AP could lower the activation energy for both decomposition steps, allowing them to occur closer together in temperature. This finding aligns with experimental data by Yuan et al. (2021), which showed that catalysing AP with Ni and Fe₂O₃ resulted in the merging of 2 exothermic peaks. The qualitative data from the DSC curve has been tabulated in Table 4.7 to illustrate the changes in LTD and HTD across all KMnO₄/AP CSP samples.

Table 4.7: Low-temperature decomposition (LTD), high-temperature decomposition (HTD) and heat release (ΔH) result of AP and KMnO₄/AP-based CSP with different ratios

Sample	LTD/°C	HTD/°C	ΔH (J/g)
AP CSP	300.18	392.10	1929.1
KMnO ₄ /AP (20:80)	-	352.34	2319.8
KMnO ₄ /AP (40:60)	-	331.32	3721.2

Table 4.7: (continued)

Sample	LTD/°C	HTD/°C	ΔH (J/g)
KMnO ₄ /AP (60:40)	300.02	382.73	1876.0
KMnO ₄ /AP (80:20)	351.21	419.82	1862.3

In addition, the merged exothermic peak in the KMnO₄/AP CSP (20:80) and KMnO₄/AP CSP (40:60) samples resulted in a shift of the HTD of AP CSP from 392.10°C to 352.34°C and 331.32°C, respectively. The KMnO₄/AP CSP (40:60) sample exhibited the most significant catalytic effect to the KMnO₄/AP CSP (20:80) sample, followed by the KMnO₄/AP CSP (60:40) and KMnO₄/AP CSP (80:20) samples. This is because it achieves the most significant reduction in the HTD value of AP, which is the primary stage of the AP CSP decomposition process. According to Table 4.7, the KMnO₄/AP CSP (20:80) and KMnO₄/AP CSP (40:60) samples did not exhibit LTD due to the merging of the two exothermic peaks. Besides, the KMnO₄/AP CSP (60:40) sample reduced the LTD and HTD of AP CSP by 300.02°C and 382.73°C, respectively. However, the KMnO₄/AP (80:20) sample showed opposite results, increasing both the LTD and HTD of AP CSP from 300.18°C and 392.10°C to 351.21°C and 419.82°C, as illustrated in Table 4.7.

The decrease in HTD indicated that KMnO₄ acted as a catalyst, providing an alternative reaction pathway with a lower activation energy barrier. Park et al. (2020) mentioned that by lowering this barrier, the catalyst facilitated the decomposition reaction of AP, enabling it to occur at lower temperatures. This effect was evidenced by the increased heat release value of the KMnO₄/AP

CSP (40:60) sample, which increased from 1929.1 J/g to 3721.2 J/g. This rise in heat release value made the overall system more prone to decomposition at lower temperatures (Cegla et al., 2019). Moreover, the merging of the two exothermic peaks, previously mentioned, resulted in a significantly high heat release. This released heat could locally increase the temperature of the reaction, further accelerating the decomposition process. Thus, it was suggested that the KMnO_4/AP CSP (40:60) sample provided the most effective catalytic performance as a dual oxidiser in the AP-based CSP system.

4.5 Heat of Combustion Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO_4/AP) Based

4.5.1 Energetic Properties (Density and Heat of Combustion) of Composite Solid Propellant (CSP) with A Dual Oxidiser (KMnO_4/AP) Based

An effective propellant formulation aimed to maximise heat release to achieve the highest possible specific impulse (I_{sp}), which measures the rocket motor's efficiency. Higher heat release contributes to higher I_{sp} and, consequently, improved overall performance. Table 4.8 summarised the impact of KMnO_4 on the heat of combustion in AP-based CSP and the combustion efficiency calculation were presented in Appendix B1.

Table 4.8: Effects of KMnO_4 with different ratios on the energetic properties of AP-based CSP

CSP Samples	Mass of the samples(g)	Heat of combustion (cal/g)	Combustion efficiency (%)
AP	28	1247	99.70
KMnO_4/AP (20:80)	28	1250.98	99.9
KMnO_4/AP (40:60)	28	1254.01	100.2
KMnO_4/AP (60:40)	28	1249.65	99.8
KMnO_4/AP (80:20)	28	1247.73	99.6

The data presented in Table 4.8 showed that all samples had a constant heat of combustion value, ranging from 1247.0 cal/g to 1247.73 cal/g. The heat of combustion for CSP samples slightly increased with the incorporation of KMnO_4 into AP up to a ratio of 40:60. However, at ratios of 60:40 and 80:20, the heat of combustion values decreased to 1249.65 cal/g and 1247.73 cal/g, respectively. Besides, the highest heat of combustion value was found in the KMnO_4/AP sample with a ratio of 40:60. Hence, this sample exhibited the highest combustion efficiency percentage, reaching 100.2 % compared to the other samples. This means that the KMnO_4/AP (40:60) sample has a higher energy release, resulting in higher temperatures and pressures within the combustion chamber and higher exhaust velocities. This is because the exhaust velocity is directly related to the energy released during combustion (Boulkadid et al., 2020). Moreover, a higher heat of combustion means more energy is available per unit mass of fuel, enhancing the propulsion's efficiency.

4.6 HCl Concentration Analysis in Combustion Product of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO₄/AP) Based

4.6.1 HCl Concentration Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO₄/AP) Based

The water samples in Figure 4.17 (a), collected using the gas bubbling method, were observed to be clear in colour as the water used is distilled water. Figure 4.17 (b) shows that the water samples turned yellowish after adding two drops of K₂CrO₄. Then, the result of the endpoint titration, as in Figure 4.17 (c), noticed the formation of a reddish-brown colour. All samples in this research exhibited the same colour change in the water samples, although the number of drops of silver nitrate required until the appearance of reddish-brown varied.

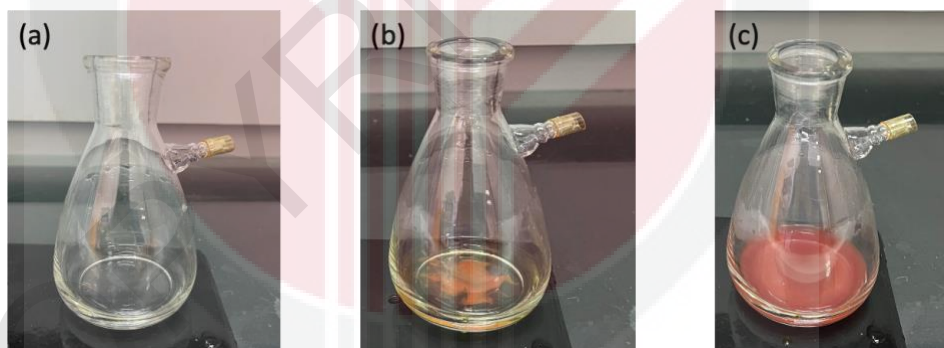
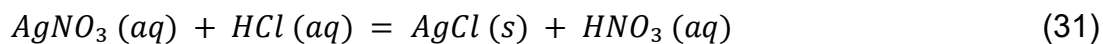
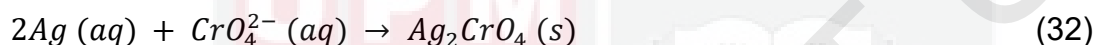


Figure 4.17: The result of the water sample at (a) initial, (b) Mid, (c) end point of Mohr's titration

The relevant stoichiometry involves the reaction between HCl and AgNO₃ in the titration method. Theoretically, when titrating hydrochloric acid (HCl) with silver nitrate, the chloride ions from HCl react with silver ions (Ag⁺) from silver nitrate to form a precipitate of silver chloride (AgCl). The reaction between silver nitrate and hydrochloric acid is as follows:

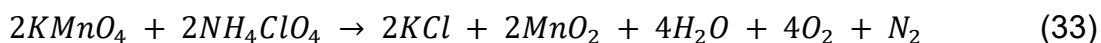


The stoichiometric ratio is 1:1, meaning 1 mole of HCl reacts with 1 mole of AgNO₃ to produce 1 mole of AgCl and 1 mole of HNO₃. AgNO₃ solution was added constantly by dropping it from the pipette dropper until the first permanent reddish-brown colour appeared. This colour change indicates the formation of silver chromate (Ag₂CrO₄), marking the end point of the titration. The endpoint is detected by the formation of a reddish-brown precipitate of silver chromate (Ag₂CrO₄) as follows:



This reaction occurs after all the chloride ions have reacted with silver ions to form silver chloride (AgCl). When KMnO₄ reacted with AP, the reaction was a highly exothermic oxidation-reduction or redox reaction. This reaction produced various compounds by decomposition and recombining the elements present in the reactants. Runtu et al. (2023) reported the same findings in experimental works, where dual oxidisers AN/AP and ADN/AN resulted in exothermic reactions. This high energy release per unit mass, or high specific energy, makes AP-based CSP especially effective for generating thrust in rocket motors and missiles. The rapid release of gases and heat produces high-pressure and high-temperature combustion products, providing the necessary thrust. The exact stoichiometry could vary depending on the reaction conditions, such as temperature, pressure, and the proportions of the reactants. The reaction served as a classic example of a redox reaction, with KMnO₄ acting as the oxidising agent and NH₄ClO₄ providing both fuel and

additional oxidiser components. The stoichiometry equation of the reaction between KMnO_4 and AP during the combustion process is as follows:



The newly developed dual oxidiser KMnO_4/AP altered only the physical structure of both compositions without affecting the chemical elements. Consequently, from the stoichiometry reaction, the combustion of the dual oxidiser KMnO_4/AP with 2 mol of KMnO_4 and 2 mol of AP produced 2 mol of potassium chloride (KCl), 2 mol of manganese dioxide (MnO_2), 4 mol of water (H_2O), 4 mol of oxygen gas (O_2), and 1 mol of nitrogen gas (N_2). KCl has a high melting point of about 770°C (1420°F). The potassium (K) in KMnO_4 scavenges the HCl to form KCl. Usually, in AP-based CSP systems, combustion temperatures mainly reach about 1500°C to 2500°C , potentially reaching or exceeding the melting point of KCl. Thus, it will be in the form of gas. The Cl elements in the combustion of KMnO_4/AP originate from KCl, which this element is not considered a highly toxic gas (Boulangé et al., 2018) compared to HCl gases, which the conventional AP-based CSP produces. Interestingly, the theoretical reaction equation in (33) suggests that this novel KMnO_4/AP dual oxidiser does not generate any HCl gases, rendering the rocket motor's combustion from this formulation safe due to meeting allowable HCl exposure limits. However, the complexity of the combustion process may result in the emission of chlorine gases (Cl_2) and trace amounts of HCl. Therefore, this study determined and compared the chloride content in the HCl from conventional AP-based CSP and the KCl from the novel KMnO_4/AP CSP samples. This determination is crucial because it accounts for all chlorine-

containing species in the combustion products, including any formed HCl or KCl that might have dissolved in water or reacted with other combustion products to form chloride salts (Chen et al., 2023). The data results of the chloride content from Mohr's titration method were tabulated in Table 4.9, and the calculations were given in Appendix B2.

Table 4.9: Result of chlorine content from the Mohr's titration method

CSP Samples	Volume level of silver nitrate solution used (mL)	Average volume level of silver nitrate solution used (mL)	Chloride content (ppm)
AP	2.16 2.01 2.13	2.1	745.5
KMnO ₄ /AP (20:80)	1.95 1.94 1.90	1.93	685.15
KMnO ₄ /AP (40:60)	1.31 1.28 1.25	1.28	454.41
KMnO ₄ /AP (60:40)	1.12 1.10 1.08	1.10	390.54
KMnO ₄ /AP (80:20)	0.92 0.81 0.90	0.87	311.22

Table 4.9 shows that the chlorine content value of all samples fell within the approximate range of 300 to 1000 ppm. The CSP sample without KMnO₄ showed the highest chlorine content at 745.5 ppm compared to the others. The incorporation of KMnO₄ into the AP-based CSP system led to a noticeable reduction in chlorine content as the ratio of KMnO₄ to AP increased. At a ratio of 60:40, the chlorine content shows a significant decrease, as the value is reduced to nearly double from the conventional AP-based CSP with a value of

390.54 ppm. Besides, the KMnO_4/AP sample with a KMnO_4 to AP ratio of 80:20 resulted in the highest reduction in chlorine content with a value of 311.22 ppm. Table 4.10 illustrates the percentage reduction in chlorine content value for the KMnO_4/AP CSP samples with different ratios from the conventional AP-based CSP.

Table 4.10: Percentage reduction from the pure AP CSP

CSP Sample	Chlorine content reduction (%)
AP	-
KMnO_4/AP (20:80)	8.10
KMnO_4/AP (40:60)	39.04
KMnO_4/AP (60:40)	47.62
KMnO_4/AP (80:20)	58.25

Referring to Table 4.10, it can be observed that the chlorine content reduction percentage increased with a higher ratio of KMnO_4 to AP. The sample with a KMnO_4/AP ratio of 60:40 demonstrated a significant reduction, nearly 50%, and the sample of KMnO_4/AP with a ratio of 80:20 resulted in the highest chlorine content, at 58.25%. This qualitative result from the experimental work elucidates that increasing the proportion of KMnO_4 in the propellant composition reduces chlorine content as a combustion by-product by reducing the reliance on AP, which is the main contributor to the production of HCl gas. Moreover, the chlorine content detected in the sample with a ratio of 80:20 KMnO_4/AP might come from the sublimation of KCl to form gases, along with a minimal amount of HCl produced. For example, in an experimental work done by Vellaisamy et al. (2020), the chlorine content detected in the AP/Li/Mg mixture was minimal, and a substantial amount of HCl was scavenged by Li and Mg, serving as HCl metal scavengers. The remaining chlorine content

could be attributed to the LiCl and MgCl₂ gases resulting from the high temperatures during the combustion process. A bar chart in Figure 4.18 visualised the comparison of chlorine content results from the literature study with samples in this research work.

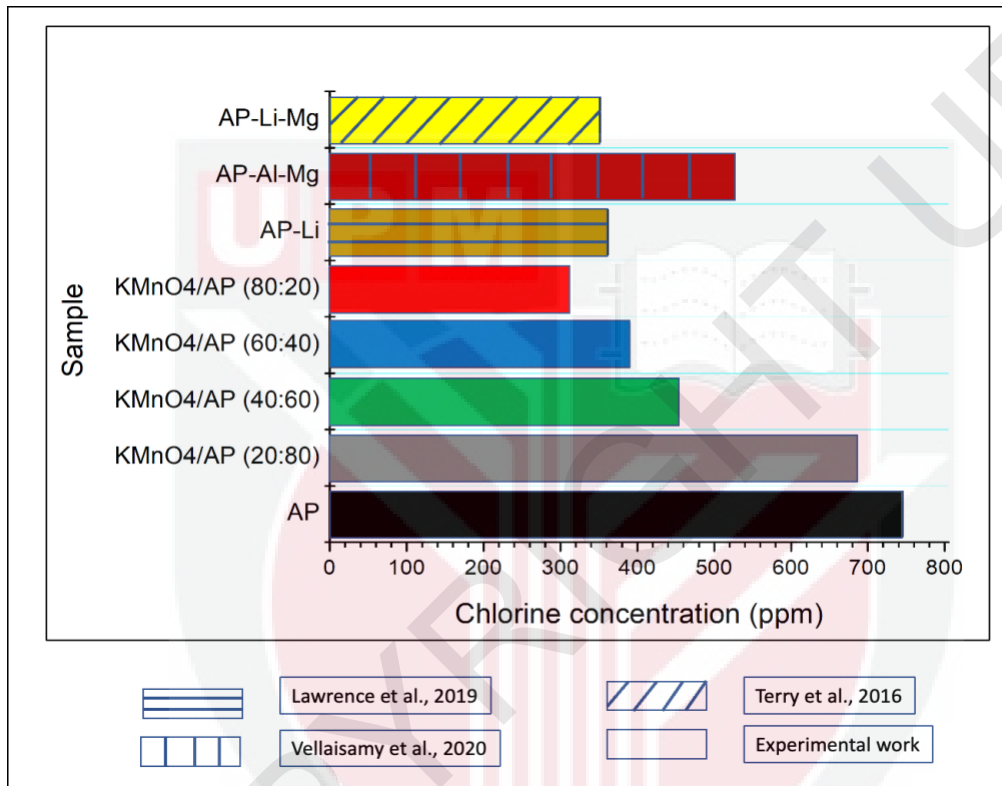


Figure 4.18: Bar chart comparison result of CSP samples chlorine concentration value in experimental work with literature

The bar chart in Figure 4.18 illustrates that certain CSP samples developed by Lawrence et al. (2019), Vellaisamy et al. (2020), and Terry et al. (2016) demonstrated a noteworthy reduction in chlorine content as a combustion by-product. The sample from this experimental work, KMnO₄/AP with a KMnO₄ to AP ratio of 60:40, exhibited a chlorine concentration nearly similar to that of the AP-Li-Mg sample produced by Terry et al. (2016). Interestingly, the KMnO₄/AP sample with a ratio of 80:20 resulted in a significantly lower chlorine

concentration in comparison to all other samples and approximately doubled from the conventional AP-based CSP. Although lithium-based propellant samples demonstrate superior performance compared to others, they were not classified as green propellants due to the emission of toxic lithium chloride as one of their exhaust products. Additionally, the handling of highly reactive lithium-based propellants presented substantial challenges. The novel KMnO_4/AP composition with a ratio of 80:20 emerged as a practical choice for dual oxidiser CSP formulations, attributing to its minimal chlorine content as a combustion by-product, with KCl emissions not classified as a toxic gas (Ebrahimi et al., 2021).

4.7 Uniaxial Properties Testing Analysis of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO_4/AP) Based

4.7.1 Stress-Strain Behaviour of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO_4/AP) Based Sample

Figure 4.19 depicts the tensile test results at various temperature conditions for all CSP samples. The temperature varied at low temperatures of 20°C and 30°C and high temperatures of 40°C, 50°C, and 60°C. Additionally, for each test, the specimens were pre-conditioned for at least three hours in an external conditioning chamber with humidity (20-25%), similar to the experimental works done by Boshra et al. (2021). The specimen was held in an environmental chamber during each test to keep the desired temperature until the testing was finished.

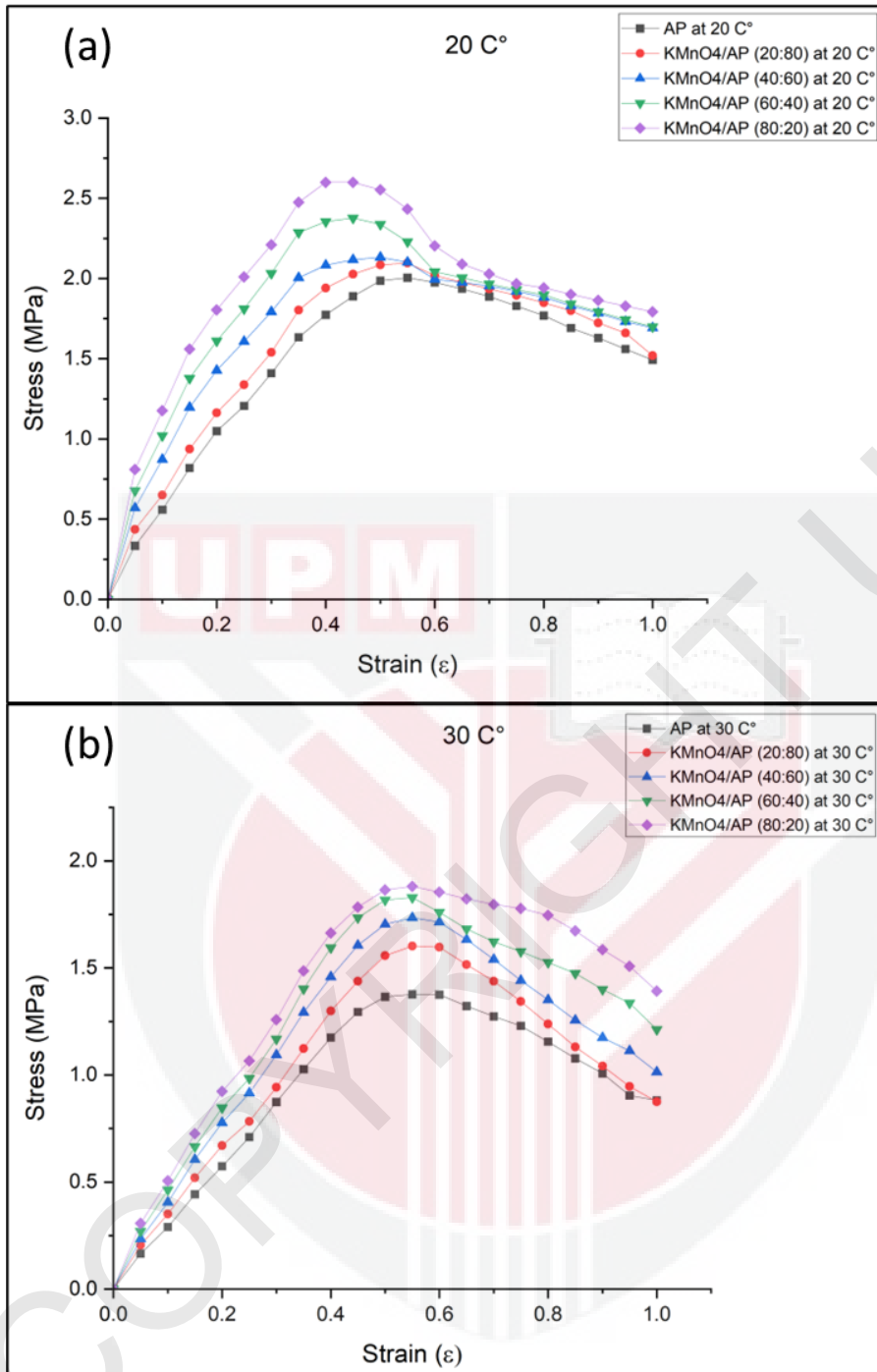


Figure 4.19: Stress-strain behaviour of CSP samples (a) AP, (b) KMnO₄/AP (20:80), (c) KMnO₄/AP (40:60), (d) KMnO₄/AP (60:40), (e) KMnO₄/AP (80:20) at different temperatures

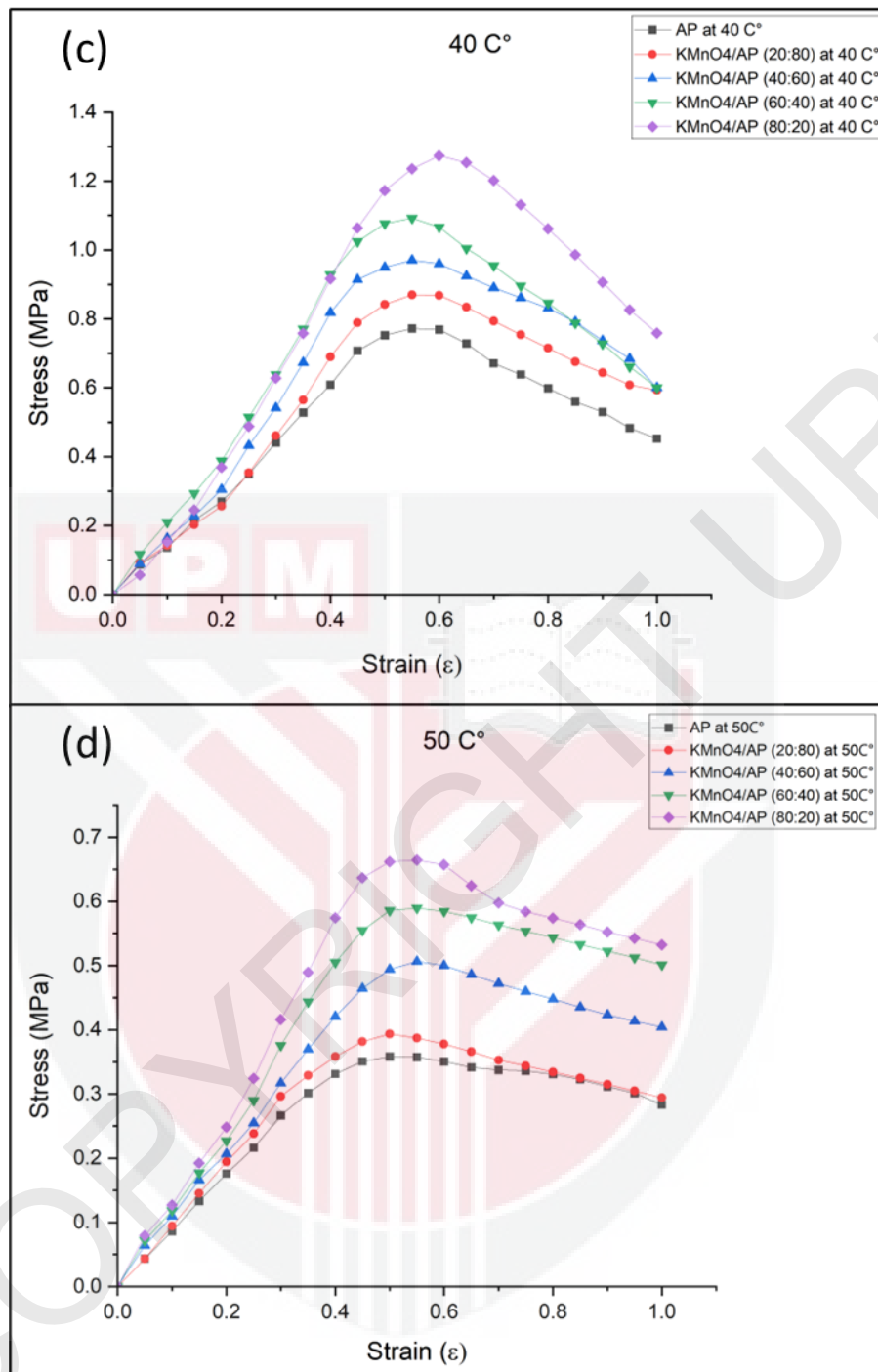


Figure 4.19: (continued)

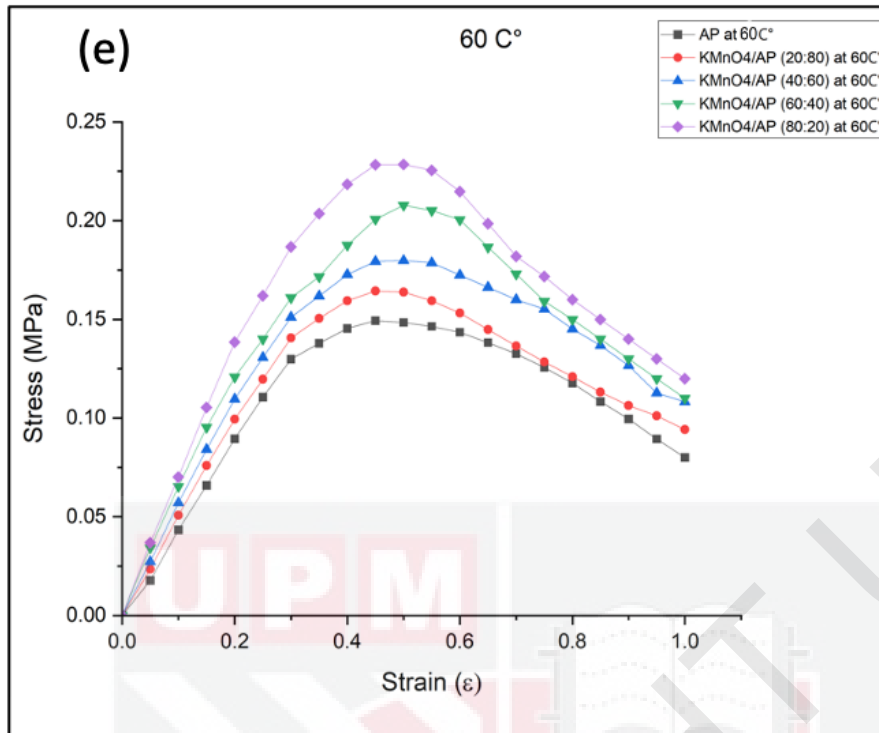


Figure 4.19: (continued)

As shown in Figure 4.19, all the CSP samples exhibited typical behaviour of the thermosetting polymer matrix in the stress curves. Initially, there was a linear elastic region with a high modulus of elasticity. This was followed by a peak at the ultimate tensile strength (UTS) with minimal plastic deformation and a sharp drop indicating brittle fracture upon reaching UTS. The stress-strain curves began with a relatively straight phase before displaying an abrupt bend, after which the stress gradually increased across a significant strain range until rupture. At a temperature of 20°C in Figure 4.19 (a), all samples have UTS values in the range of 2 to 2.7 MPa, suggesting increased stiffness within this temperature regime. This can be proved by an experimental work reported by Pimont et al. (2019), which stated that low temperature reduces the mobility of polymer chain molecules. This slows down the relaxation of the stress, resulting in a higher stress response. As temperature increases, a

decrease in UTS values was noted for all samples, with the KMnO_4/AP (80:20) sample maintaining the highest UTS, followed by the KMnO_4/AP (60:40), KMnO_4/AP (40:60), KMnO_4/AP (20:80), and AP samples.

Besides, it clearly shows the effect of temperature on stress and strain. As the temperature decreased, stress levels increased. The impact of temperature and the KMnO_4 to AP ratio on the UTS, Young's modulus and maximum elongation will be discussed in detail in the following subchapter. Generally, during the tensile test, failure occurs near a solid particle within the binder or due to the bonding failure between some fillers and the binder. When vacuum holes or pores are formed on the propellant sample, their size grows as the stress/strain rises. According to Xu et al. (2008), when these vacuum holes reach a large size (several micrometres), they generate micro failures, which initiate microscopic cracks in the binder and cause the specimen to collapse. The strain values for all the samples at all temperatures were tabulated in Table 4.11

Table 4.11: Sample comparison of stress and maximum elongation value of CSP samples at different temperatures and KMnO_4 to AP ratio

Sample	Stress (MPa) at $\epsilon = 0.5$					Maximum elongation (ϵ)				
	20°C	30°C	40°C	50°C	60°C	20°C	30°C	40°C	50°C	60°C
AP	2.03	1.50	0.80	0.39	0.15	5.43	4.08	3.85	3.01	2.73
KMnO_4/AP (20:80)	2.33	1.73	0.90	0.40	0.17	5.41	3.97	3.84	2.99	2.67
KMnO_4/AP (40:60)	2.50	1.80	1.05	0.54	0.19	5.40	3.67	3.63	2.91	2.50
KMnO_4/AP (60:40)	2.91	1.98	1.21	0.60	0.22	5.12	3.41	3.27	2.59	2.32
KMnO_4/AP (80:20)	3.15	2.00	1.36	0.75	0.25	5.00	3.55	3.11	2.45	2.15

The tensile strength behaviour of propellants was observed to change at low temperatures due to structural changes in the binder. When the temperature drops, the polymeric chain's mobility changes significantly, and it enters a phase known as the glass transition. Kosiba et al. (2017) reported that the physical and mechanical characteristics of the polymer are dramatically transformed due to this effect. Besides, the HTPB binder behaves more rigidly due to reduced molecular mobility, limiting the material's capacity to stretch. Figure 4.20 shows the physical state of the dog bone samples after undergoing a uniaxial tensile test.



Figure 4.20: Physical state of dog bone samples after uniaxial tensile test

As the temperature falls, the elastic modulus increases significantly with more forces needed to break the polymer chain of the binder, thus making the sample break. This can be illustrated in Table 4.11 as the stress value at an elongation of 0.5 for sample KMnO_4/AP (80:20) decreases from 3.15 MPa to

0.25 MPa from 20°C to 60°C, respectively. This is also observed in all the samples, including the pure AP with no KMnO_4 .

Moreover, it can be observed that the elongation decreases with increased temperature for all the samples. It can be noticed that the maximum elongation value of the sample KMnO_4/AP (80:20) decreases from 5.0 to 2.15 from the temperature of 20°C to 60°C, respectively. Besides, the highest value of maximum elongation was noticed in the sample of pure AP with a value of 5.43, followed by samples KMnO_4/AP (20:80), KMnO_4/AP (40:60), KMnO_4/AP (60:40), and KMnO_4/AP (80:20) with value 5.41, 5.40, 5.12, and 5.0 respectively at 20°C. This finding also shows that with the increased ratio of KMnO_4 to AP, the maximum elongation decreases, and this incorporation of KMnO_4 makes the AP-based CSP mechanical properties become stiffer. The same findings are observed in experimental works by Kim et al. (2019), in which they reported that higher temperatures increase the mobility of polymer chains, leading to a more pronounced viscoelastic behaviour. This increased mobility allows the chains to slide past one another more efficiently, reducing the material's ability to stretch without breaking.

4.7.2 Factorial Design in RSM of Composite Solid Propellant (CSP) with Dual Oxidiser (KMnO_4/AP) Based Sample

This investigation aimed to determine and identify the significant factors that mainly influence the tensile strength of CSP samples. The experiment was run in a randomised order using MINITAB. The design matrix of uncoded factors

and response, which is the tensile strength, is given in Appendix B3. Factors of V_1 and V_2 represent temperature and KMnO_4 to AP ratio, respectively.

4.7.2.1 Statistical Analysis in Uniaxial Tensile Properties Testing

Coefficients of regression standardised effect of the factors and interactions and p-values of the impact results are shown in Table 4.12. Complete statistical results for this study are presented in Appendix B4.

Table 4.12: Estimated effects and coefficient for tensile strength

Term	N	Coefficient	SEC	SE	P
Constant		8.300	0.913	90.90	0.000
Temperature ($^{\circ}\text{C}$)	V_1	-3.086	0.634	-48.4	0.000
Ratio KMnO_4 to AP	V_2	1.103	0.634	-17.38	0.000
Temperature ($^{\circ}\text{C}$) * Temperature ($^{\circ}\text{C}$)	V_1*V_1	3.940	0.459	0.86	0.397
Ratio KMnO_4 to AP * Ratio KMnO_4 to AP	V_2*V_2	-8.560	0.459	-1.87	0.071
Temperature ($^{\circ}\text{C}$) * Ratio KMnO_4 to AP	V_1*V_2	-4.200	1.100	-0.38	0.707
$R^2 = 0.989$	$R^2 (\text{adj}) = 0.986$				

N = Notation; SEC = Standard error of coefficient; SE = Standardized effect

The P in Table 4.12 was important in determining the significance of the effects in the model. With the confidence level set at 95% ($P < 0.050$), the effect was considered statistically significant. All individual and interaction effects were significant at a 95% confidence level. The effect of V_2 was highly significant with $P < 0.000$, while that of " V_1*V_2 " was not significant with $P < 1.0$. The values for R^2 of 0.989 and R^2 (adjusted) of 0.986 were high, indicating a good fit for

the model, with 98.9% of the results explainable. The model also showed high dependence and correlation between the observed and the predicted response values.

4.7.2.2 Regression Model of Uniaxial Tensile Properties Testing

Using coefficient and terms from Table 4.12, the regression model developed as shown in Equation 34, where YTS is the response of tensile strength, V_1 is temperature, and V_2 is KMnO₄ to AP ratio.

$$\begin{aligned} \text{YTS} = & 3.596 - 0.0742 (V_1) + 0.00910 (V_2) + 0.000157 (V_1V_1) - 0.000021 (V_2V_2) \\ & - 0.000042 (V_1*V_2) \end{aligned} \quad (34)$$

4.7.2.3 Pareto Plot of Uniaxial Tensile Properties Testing

Figure 4.21 displayed the Pareto plot of the standardised effects, revealing that both temperature (V_1) and the KMnO₄ to AP ratio (V_2) were the most influential factors for tensile strength, as these factors extended well beyond the reference line. Besides, temperature (V_1) emerged as a more significant factor affecting the tensile strength value more than the KMnO₄ to AP ratio (V_2).

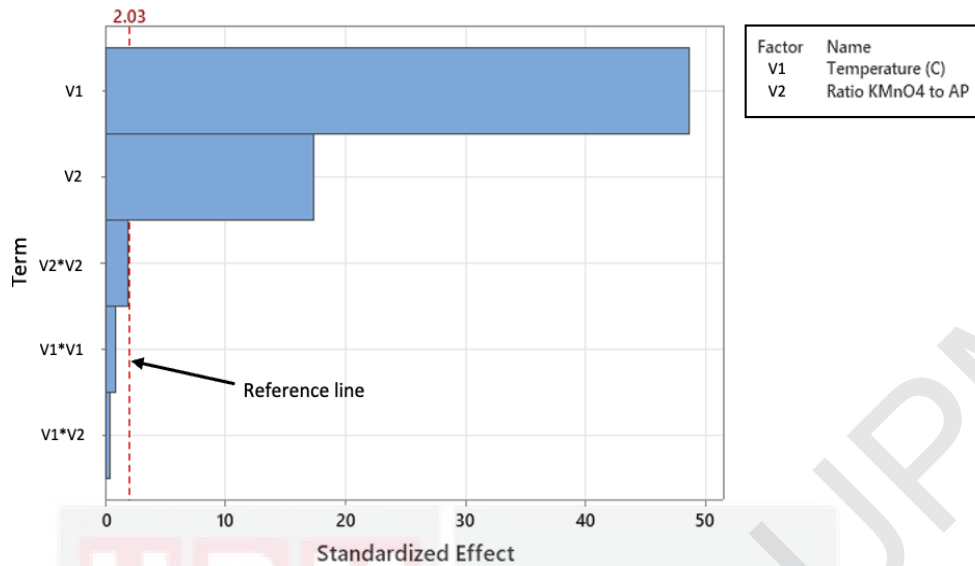


Figure 4.21: Pareto plot of the standardised effects on tensile strength

4.7.2.4 Normal Probability Plot of Residual in Uniaxial Tensile Properties Testing

This residual plot was drawn to test the normality of the data set, as shown in Figure 4.22. If the points had fallen further from the straight line, it indicates a more significant departure from normality. Most of the points fell close to the straight line, with very few points that were distant from the line. Therefore, it was concluded that the experimental data set used for the statistical analysis originates from a normally distributed population.

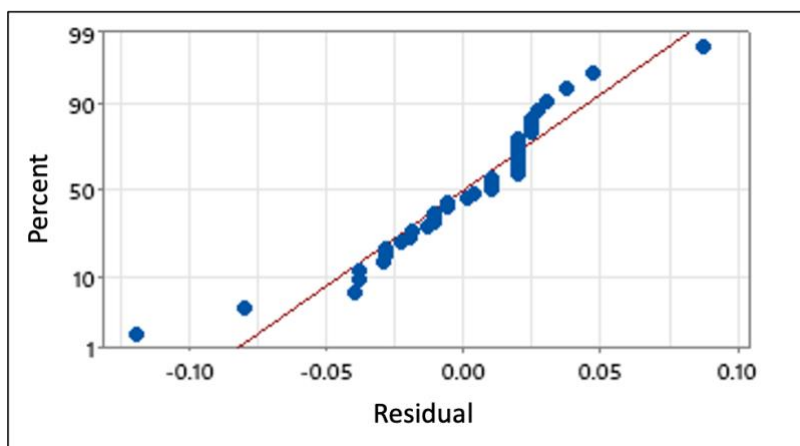


Figure 4.22: Normal probability plot of the residual data for tensile strength

4.7.3 Response Surface Methodology (RSM) of Uniaxial Tensile Properties Testing

This study aimed to determine the significance of each factor, namely temperature (V_1) and KMnO_4 to AP ratio (V_2), as well as their interactions, to elucidate the relationship between the factors and the response under tensile forces. It aimed to optimise the interacting factors to achieve the maximum tensile strength of CSP samples. Since KMnO_4 was introduced into AP-based CSP in this study, ensuring the safety and reliability of these systems was paramount. Besides, the testing helped evaluate solid propellants' strength, durability, and behaviour under various conditions, which is crucial for designing safe and reliable propulsion systems. The example of the design matrix and response values for the sample are shown in Table 4.13.

Table 4.13: Design matrix and response values for uniaxial tensile test

Run	Coded factor		Uncoded factor		Response
	Temperature (V ₁)	KMnO ₄ to AP ratio (V ₂)	Temperature (V ₁)	KMnO ₄ to AP ratio (V ₂)	Tensile strength (MPa)
1	0	-2	45	0	0.60
12	-1	-1	40	20	0.98
21	2	0	55	40	0.20
39	1	1	50	60	0.67

4.7.3.1 Effect of Factors on Tensile Strength, Maximum Elongation, and Young's Modulus Properties

ANOVA and regression models were utilised to analyse the effect of various factors on the mechanical properties of the CSP samples. Contour plots were used for better illustration. Figure 4.23 illustrates the effect of temperature and ratio of KMnO₄ to AP on tensile strength. Tensile strength increased with higher values of ratio KMnO₄ to AP and lower value of temperature. Higher tensile strength of more than 2.0 MPa was observed at the range of 20°C to 30°C for temperature and 40°C to 80°C for ratio KMnO₄ to AP.

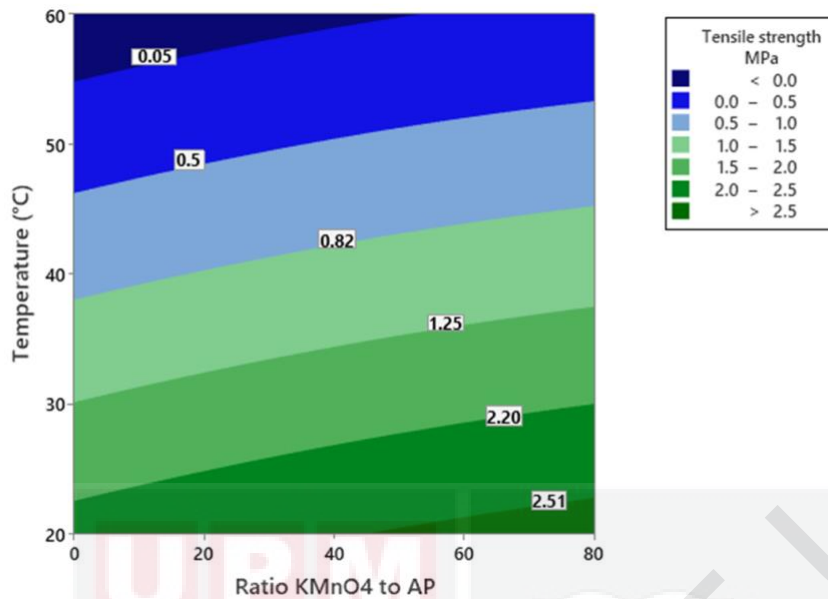


Figure 4.23: Contour plot for the effect of the ratio of KMnO_4 to AP and temperature on the tensile strength properties of CSP

The KMnO_4 to AP ratio also has a strong effect on tensile strength. However, the effect of temperature acted differently for the sample with brittle and ductile behaviour. Figure 4.23 demonstrated that samples with a temperature higher than 40°C exhibited ductile behaviour. In comparison, samples with a temperature value lower than 40°C exhibited brittle behaviour with a tensile value of more than 1.0 MPa. With decreasing temperature, a higher KMnO_4 to AP ratio produced higher tensile strength. At an 80:20 ratio of KMnO_4 to AP, a higher temperature of 60°C produced a tensile strength of nearly 0.5 MPa. When the temperature was decreased to 20°C , tensile strength was also elevated to over 2.5 MPa. The effect of temperature and KMnO_4 to AP ratio on maximum strain was also plotted and presented in Figure 4.24.

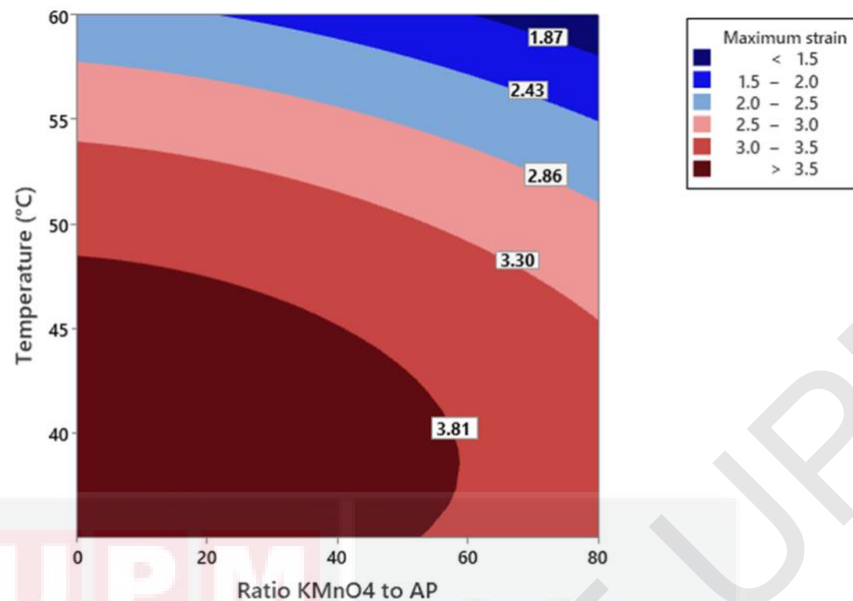


Figure 4.24: Contour plot for the KMnO₄ to AP ratio and temperature on the maximum strain of CSP samples

Based on Figure 4.24, It is noticed that the maximum strain increased with lower values of ratio KMnO₄ to AP and at lower values of temperatures. At the range of over 3.0, maximum strain was observed at 55°C to 40°C for temperature and at all KMnO₄ to AP ratio. The temperature significantly affects this maximum strain value compared to the KMnO₄ to AP ratio, which does not give much difference. This is because as temperature increases, the polymer matrix in the solid propellant begins to soften. This reduces the material's ability to sustain elongation under stress, as the softened polymer chains can no longer maintain their structure and integrity as effectively. The surface plot in Figure 4.25 clearly illustrates the relationship between the temperature and KMnO₄ to AP ratios on the maximum strain of CSP samples.

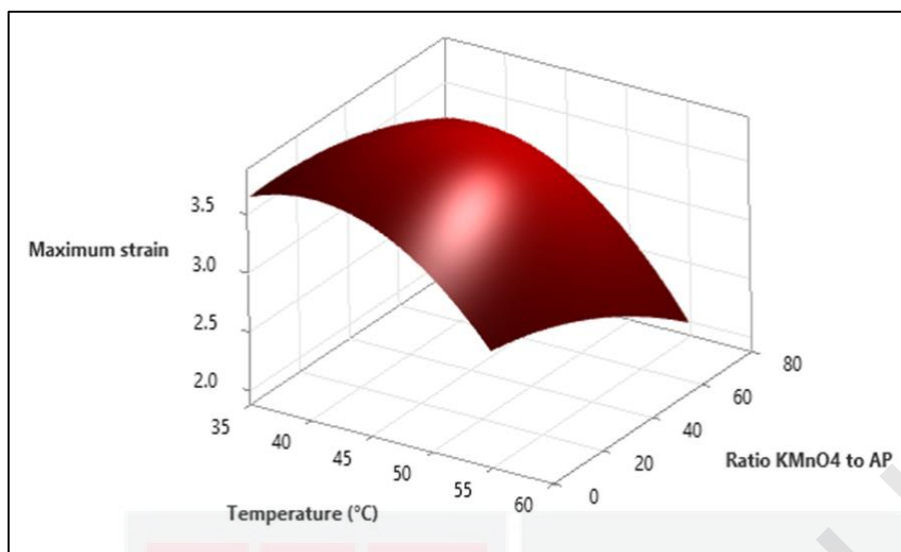


Figure 4.25: Surface plot of KMnO₄ to AP ratio and temperature for the maximum strain value

With reference to the surface plot in Figure 4.25, it is confirmed with the contour plot in Figure 4.24 that the high maximum strain is produced at the temperature of below 55 °C and at all KMnO₄ to AP ratios. Besides, reports by Kumar et al. (2019) claimed that the high elongation at the lower temperature is due to the phase transition of polymer binder. Some components in the CSP systems, especially the polymer binder, may undergo phase transitions at elevated temperatures. For instance, a transition from a rubbery state to a more viscous or even liquid state can significantly diminish the elongation capacity of the material. Thus, the KMnO₄ to AP ratio does not have a highly significant effect on the strain value for the samples, but it contradicts the tensile strength and Young's modulus value. Figure 4.26 shows a contour plot of the KMnO₄ to AP ratio and temperature effect on the Young's modulus value for all the tested samples.

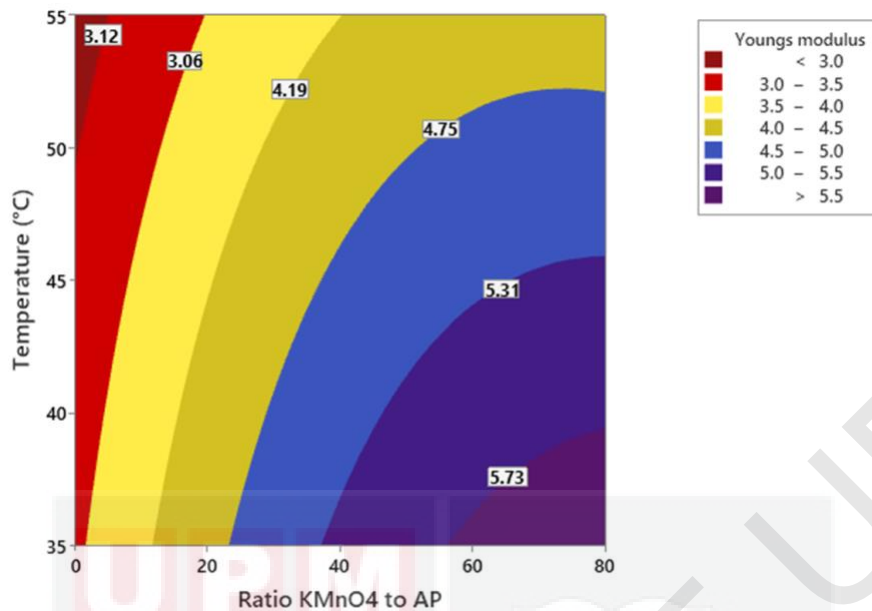


Figure 4.26: Contour plot for the KMnO₄ to AP ratio and temperature on Young's Modulus

Young's modulus, also known as the elastic modulus of an AP-based CSP, quantifies the material's stiffness, indicating how much it will deform under a given load. Specifically, it is the ratio of stress (force per unit area) to strain (proportional deformation) in the linear elastic region of the material's stress-strain curve. As shown in Figure 4.26, the contour plot clearly illustrates the effect of temperature and KMnO₄/AP ratio on Young's modulus of all the CSP samples. From the plot, it is observed that with decreasing temperature, a higher KMnO₄ to AP ratio exhibited higher Young's modulus for all samples. Pure AP with KMnO₄ to AP ratio of 0 shows the least value of Young's modulus at high temperature with a value of about 3.12 MPa. When increasing the KMnO₄ content up to 80:20 ratio, this ratio of stress to strain increases to around 5.73 MPa. The relationship between the two factors on the young's modulus can be illustrated clearly using surface plot in Figure 4.27.

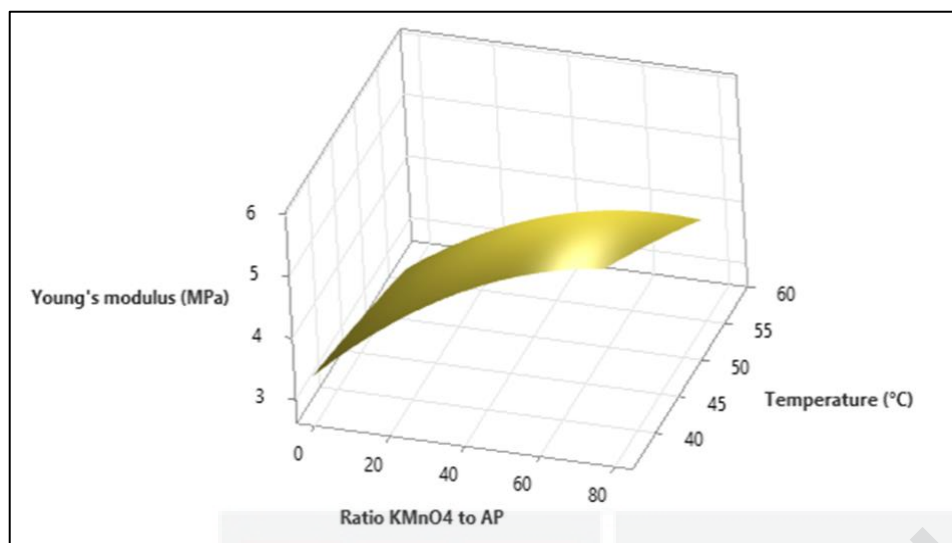


Figure 4.27: Surface plot of temperature and KMnO_4 to AP ratio for Young's modulus

The surface plot in Figure 4.27 clearly describes the relation between temperature and KMnO_4/AP ratio on Young's modulus of CSP samples. The peaks (high points) and valleys (low points) on the surface plot indicate the optimal or suboptimal values of Young's modulus effect from temperature and the KMnO_4/AP ratio. Besides, the shape of the surface shows the interactions between the temperature and KMnO_4 to AP ratios. The curve shape is noticed to indicate that the temperature and KMnO_4 to AP ratio are a significant interaction between the variables. Furthermore, this surface plot also proved the contour plot result in Figure 4.26, in which Young's modulus is maximum at the low temperature and high KMnO_4 to AP ratio. The findings are concurrent with an explanation reported by Adel et al. (2011) that many polymers used in solid propellants exhibit a transition from a rubbery to a glassy state as the temperature decreases. Below glass transition temperature (T_g), the polymer is in a glassy state, characterised by higher stiffness and

brittleness. In the glassy state, the material's Young's modulus is significantly higher than in the rubbery state.

4.7.4 Summary

The objective of this study was to determine the effect of KMnO_4 to AP ratio on the tensile, maximum strain, and Young's modulus at different sample temperature conditions. Besides, the RSM method was used to identify the significant factors that mostly influence the tensile strength of CSP samples. Results showed that all individual and interaction effects were significant at $P < 1.0$. CSP samples were very significantly affected by their temperature ($P < 0.000$), followed by KMnO_4 to AP ratio ($P < 0.000$) and by the interaction between both factors ($P < 1.0$). The tensile strength of CSP samples was greatly and positively affected by both temperature KMnO_4 to AP ratio.

As the temperature increases, the tensile strength value of the samples decreases at all KMnO_4 to AP ratios. Sample with a temperature of 20°C and KMnO_4 to AP ratio of 80:20 recorded a high tensile strength of more than 2.51 MPa. With increased temperature, the CSP samples resulted in more ductile behaviour, and the lowest tensile strength can be achieved. The KMnO_4 to AP ratio does not significantly affect the maximum strain value as the temperature influences this. The maximum strain value of CSP samples increases as the temperature decreases for all the samples, which can be attributed to the phase transition of the polymer binder. CSP samples observed the maximum Young's modulus value at the temperature of 0°C and KMnO_4 to AP ratio of 80:20 with a value of over 5.73 MPa. The increased KMnO_4 to AP ratio and

decreased temperature increased the value of Young's modulus. In this experiment, it can be concluded that the addition of KMnO_4 on AP-based CSP systems increases the tensile strength value of the propellant, which is very practical to implement in rocket motor applications as it can sustain mechanical stresses and forces during the operation.

4.8 Burn rate analysis of composite solid propellant (CSP) with dual oxidiser (KMnO_4 /AP) based sample

4.8.1 Factorial design in RSM of composite solid propellant (CSP) with dual oxidiser (KMnO_4 /AP) based sample

This investigation aimed to observe and identify the significant factors that mostly influence the burn rate properties of AP-based CSP systems. The experiment was run in a randomized order using MINITAB software. The design matrix of uncoded factors and response, which is the burn rate value, is given in Appendix B5. Factors V_1 and V_1 represent pressure and KMnO_4 to AP ratio, respectively.

4.8.1.1 Statistical Analysis in Burn Rate Test

Results for coefficients of regression and standardized effect of the factors and interactions, as well as P-values of the effects, are shown in Table 4.14. These results show the most significant factor that influences the response value the most. Complete statistical results for this study are shown in Appendix B6.

The P in Table 4.14 is important in determining the significance of the effects in the model. The effect was considered statistically significant, with the

confidence level set at 95% ($P < 0.050$), same as the uniaxial tensile test. In Table 4.14, all individual and interaction effects were shown to be significant at a 95% confidence level. The effect of V_1 was highly significant with $P < 0.000$, while that of " V_1*V_2 " was very significant with $P < 0.5$. The values for R^2 of 0.94 and R^2 (adjusted) of 0.92 were high, indicating a good fit for the model with 94% of the results explainable. The model also showed the dependence and correlation between the observed and the predicted response values because the R^2 value is still at the acceptable value, which is more than 90%.

Table 4.14: Estimated effects and coefficient for burn rate test

Term	N	Coefficient	SEC	SE	P
Constant		6.274	0.121	51.83	0.000
Pressure (atm)	V_1	0.471	0.0642	5.6	0.000
Ratio KMnO_4 to AP	V_2	-0.113	0.084	-1.34	0.189
Pressure (atm) * Pressure (atm)	V_1*V_1	-0.192	0.061	-3.15	0.003
Ratio KMnO_4 to AP * Ratio KMnO_4 to AP	V_2*V_2	-0.522	0.061	-8.57	0.000
Pressure (atm) * Ratio KMnO_4 to AP	V_1*V_2	-0.132	0.146	-0.9	0.373
$R^2 = 0.94$		$R^2(\text{adj}) = 0.92$			

N = Notation; SEC = Standard error of coefficient; SE = Standardized effect

4.8.1.2 Regression Model of Burn Rate Test

Using coefficient and terms from Table 4.14, the regression model developed as shown in Equation 35 where YBR is the response of burn rate, V_1 is pressure and V_2 is KMnO_4 to AP ratio.

$$\begin{aligned} \text{YBR} = & -1.60 + 4.54 (V_1) + 1.1251 (V_2) - 0.768 (V_1) * (V_1) - 0.001305 (V_2) * (V_2) \\ & - 0.0132 (V_1) * (V_2) \end{aligned} \quad (35)$$

4.8.1.3 Pareto Plot of Burn Rate Test

Figure 4.28 shows the Pareto plot of the standardized effects. From the chart, ($V_2 * V_2$) was found to be the most influential factor for burn rate value as the factor extends well beyond the reference line. Other factors, which also extend beyond the reference line, are statistically significant at a 95% confidence level and have smaller effects. In addition, pressure (V_1) has a higher effect on the burn rate value compared to KMnO_4 to AP ratio (V_2) as this (V_1) does not reach the reference line of 2.035.

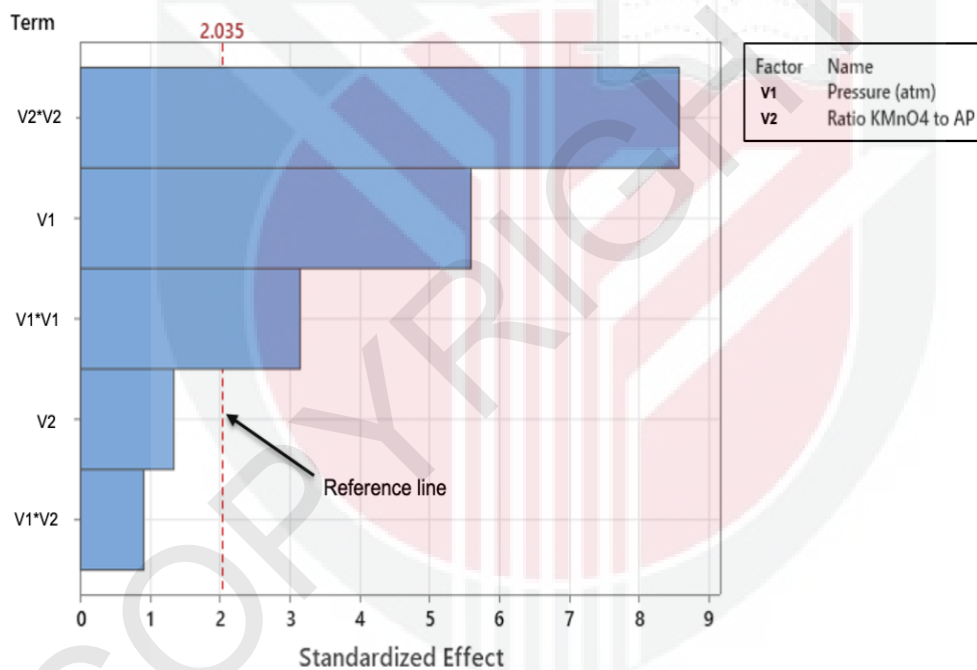


Figure 4.28: Pareto plot of the standardized effects on burn rate test

4.8.1.4 Normal Probability Plot of Residual of Burn Rate Test

To test the normality of the data set, the residual plot is drawn as illustrated in Figure 4.29. The same concept was previously explained in the past subchapter: If the points fall further from the straight line, it is an indication of

a greater departure from normality. In this experimental work, the points felt close to the straight line and only some of the points go further from the line. Therefore, the experimental data set used for the statistical analysis comes from a normally distributed population.

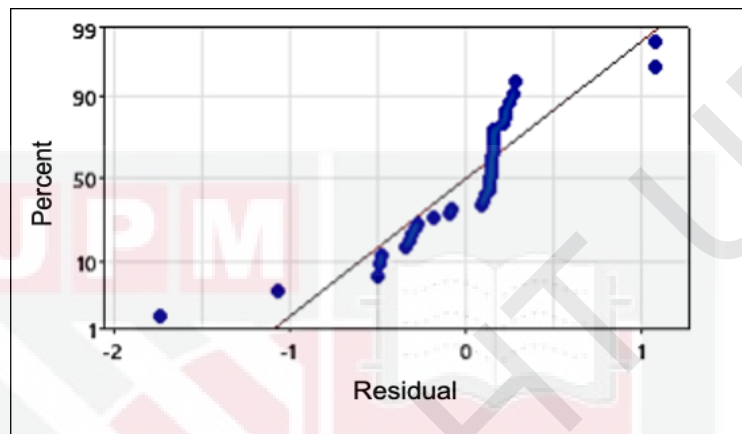


Figure 4.29: Normal Probability plot of the residual data for burn rate test

4.8.2 Response Surface Methodology (RSM) of Burn Rate Test

The objective of this study is to determine the significance of each factor which are pressure (V_1) and KMnO_4 to AP ratio (V_2), and their interactions, to elucidate the relationship between the factors and response. As this study focuses on developing dual oxidisers in AP-based CSP, the burn rate is one of the parameters that need to be evaluated to ensure the formulation of the newly developed composition is practical. The burn rate affects the internal pressure within the rocket motor. A higher-than-expected burn rate can lead to excessive pressure, potentially causing catastrophic failure. Evaluating the effect of incorporating KMnO_4 in AP-based CSP burn rate behaviour ensures that the motor operates within safe pressure limits. The example of the design matrix and response values for the sample are shown in Table 4.15.

Table 4.15: Design matrix and response values for burn rate test

Run	Coded factor		Uncoded factor		Response Burn rate (mm/s)
	Temperature (V ₁)	KMnO ₄ to AP ratio (V ₂)	Pressure (V ₁)	KMnO ₄ to AP ratio (V ₂)	
5	-1	1	2.0	0	4.79
14	1	1	1.5	20	4.75
17	1	1	2.5	60	5.70
21	-1	1	2.0	80	4.24

4.8.2.1 Effect of Factors on Burn Rate Characteristics of CSP Samples

Small propellant strands are burned in the laboratory to determine the burning rates, which are then measured by plotting the linear surface regression against time. The contour plot is displayed in Figure 4.30, together with the strand burning rate and plot computed pressure of propellant samples with varying ratios of KMnO₄ to AP that were collected under various pressure ranges. As anticipated, all propellant samples burn faster as pressure rises, and across the whole pressure range, propellants with KMnO₄/AP as a dual oxidiser in the matrix burn quicker than pure AP-based propellant samples except for KMnO₄/AP (80:20) sample. In addition, it was noticed that there was not much of an increase in burn rate value at the lower pressure range for all the samples. This can be seen in Figure 4.30; the thickness of the burn rate contour layers at the lower pressure range is smaller compared to the higher pressure. Besides, the calculations for determining the burn rate value using equation (28) were presented in Appendix B7.

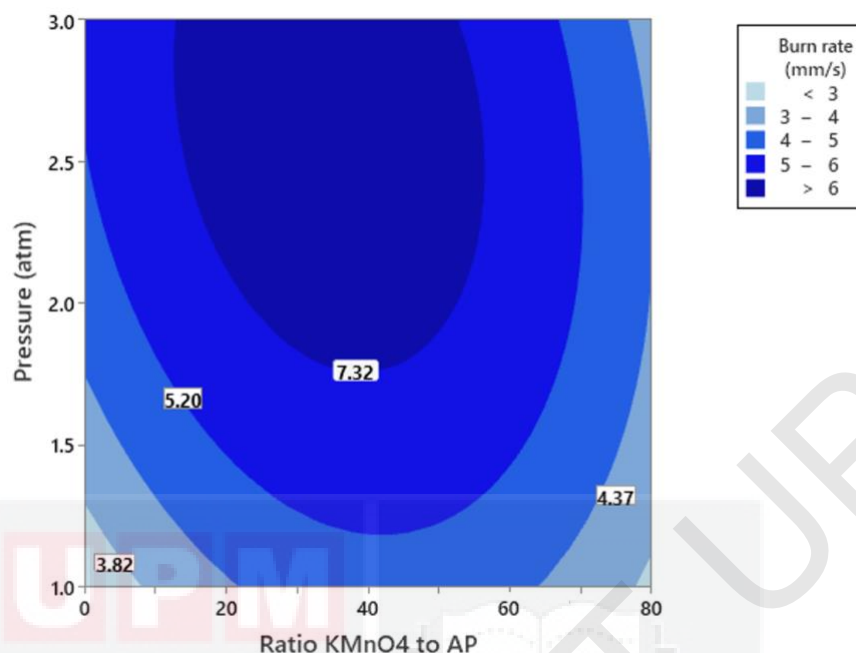


Figure 4.30: Contour plot for the effect of the ratio of KMnO_4 to AP and pressures on the burn rate characteristics of CSP samples

The results indicated that the burn rate of propellant was enhanced with the incorporation of KMnO_4 in an AP-based CSP system with certain ratios. This happens because the presence of KMnO_4 with ratios of 20:80 and 40:60 reduces the AP decomposition temperature and increases the gas phase reactions, as discussed in the previous chapter. KMnO_4 also enhances AP condensed phase reactions and reduces the binder melt layer on the burning surface. Tolmachoff et al. (2022) explained that the incorporation of a burn rate catalyst, which initially improved the thermal decomposition temperature of AP, helps in accelerating the deflagration rates of AP, hence the burning rate of propellant.

It was observed from Figure 4.30 that the CSP sample's burn rate rose as the ratio of KMnO_4 to AP increased up until 40:60 at each pressure. However, the

burn rate of the samples starts to reduce when the KMnO_4 to AP ratio increases to 80:20. This can be proved from the contour plot in Figure 4.30, which shows the blue colour is darker towards the ratio of 40:60. This also illustrates that the maximum burn rate value of the CSP samples is at the ratio of 40:60 at all pressure regimes. Besides, this contour plot can also show the most significant parameters of the CSP samples that resulted in the maximum value of burn rate, and the data is tabulated in Table 4.16.

Table 4.16: Burn rate result data of CSP samples with various pressures

CSP samples	Burn rate (mm/s) at pressures				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
AP	3.88	4.19	4.50	5.02	5.31
KMnO_4/AP (20:80)	4.31	4.75	5.69	6.00	6.31
KMnO_4/AP (40:60)	4.79	5.51	6.42	7.32	7.53
KMnO_4/AP (60:40)	4.29	4.62	5.42	5.71	6.02
KMnO_4/AP (80:20)	3.78	3.99	4.23	4.81	5.00

Based on Table 4.16, the AP-based CSP as reference formulation has burn rates ranging from 3.88 mm/s to 5.31 mm/s at testing pressures between 1 and 3 atm. The maximum burn rate resulted in the CSP sample of ratio 40:60, which was observed at 7.53 at 3 atm, followed by the CSP sample of ratio 20:80 with a value of 6.31 atm. However, the burn rate value starts to reduce when the ratio of the samples increases as the value becomes 6.02 mm/s and 5.00 in the samples of KMnO_4/AP (60:40) and KMnO_4/AP (80:20), respectively. This numerical value can strongly prove that the CSP samples of KMnO_4/AP (40:60) have the highest burn rate value at all the pressure

variations compared to other samples, and the relationship between the ratio of KMnO_4 to AP and pressures towards burn rate was illustrated in the surface plot in Figure 4.31. This result was the same as in experimental works by Tsuchiya et al. (2023), which incorporated AN and ADN in AP-based CSP. The result was that the burn rate value is maximum at the middle ratio between AN/ADN and AP, and it starts to decrease when the amount of AN/ADN is more than half.

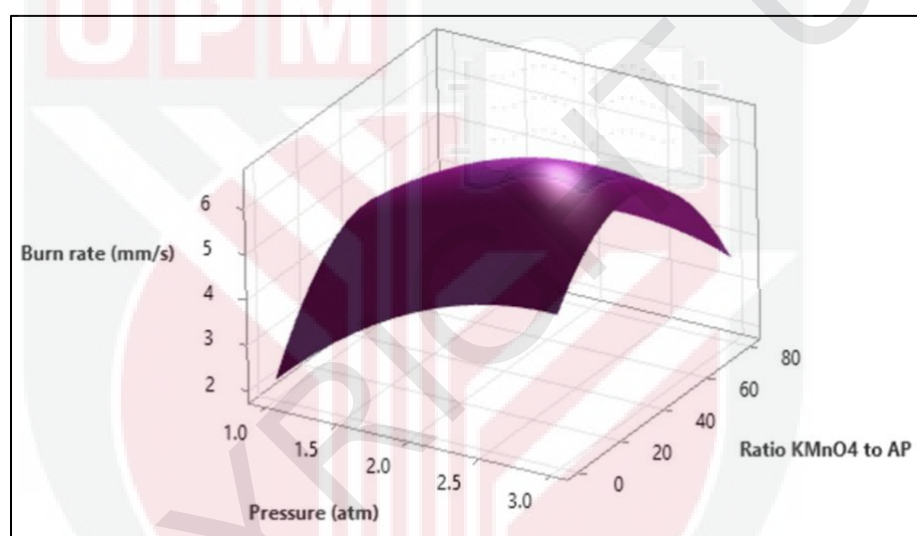


Figure 4.31: Surface plot for the effect of the ratio of KMnO_4 to AP and pressures on the burn rate characteristics of CSP samples

This finding is concurrent with the previous experimental results, such as thermal decomposition properties testing, Brunauer-Emmett-Teller (BET) surface area analysis, and heat of combustion analysis. The incorporation of KMnO_4 in AP-based CSP resulted in a specific surface area around 2 to 3 times bigger. Because of this increase, the number of surface-active sites available for the NH_3 and HClO_4 by-products of AP decomposes to adsorb and subsequently react (Akbi et al., 2022). Consequently, there was an

increase in heat transfer and burn rate due to faster gas phase processes. Furthermore, a comparison of the experimental results was made with results from other experimental works from the literature study, as shown in Table 4.17.

Table 4.17: Burn rate result validation with other studies in the development of dual oxidiser

CSP Samples	Burn rate (mm/s) at 3 atm pressures	References
AP	5.31	-
KMnO ₄ /AP (40:60)	7.53	-
AP-Fe ₂ O ₃	7.81	Fujimura et al. 2010; Kohga et al. 2019
AP/AN	4.01	Kohga et al. 2019
ADN/AN	4.52	Sims et al. 2022
AP-Ge	5.35	Ríos et al. 2019; Liu et al. 2021

As can be seen based on Table 4.17 above, AP with incorporation of ferric oxide resulted in the highest burn rate properties value at 3 atm pressure. This proved that up until now, ferric oxide has been the most promising material to be used as a catalyst for AP-based CSP burn rate enhancers. However, due to the production of toxic gases as combustion by-products, ferric oxide (Fe₂O₃) cannot be a perfect candidate for developing green materials for AP-based CSP. This is the challenge that many researchers face now. KMnO₄/AP with a ratio of (40:60) observed almost similar burn rate behaviour to the ferric oxide AP-based CSP. Besides, this KMnO₄/AP resulted in lesser HCl as a toxic gas in the combustion by-product. Hence, KMnO₄ is suggested as a good candidate to be a dual oxidiser to AP-based CSP systems.

4.8.3 Effect of Burn Rate on The Mass Flow Rate of the CSP For Solid Rocket Motor Applications Performances

As mentioned previously, the burn rate properties will directly influence the performance of the solid rocket motor due to the mass flow rate produced. The mass flow rate is known as ($\dot{m}$) is the amount of mass of the propellant being consumed per unit time, typically measured in kilograms per second (kg/s) or pounds per second (lb/s). Besides, this mass flow rate will significantly affect the value of thrust produced in static tests or dynamic tests of the rocket motor application. In this research study, the CSP samples' mass flow rate was calculated as shown in Appendix B8, and the values were tabulated in Table 4.18. The density of the CSP samples was determined using a weighting scale, and the value of the propellant sample burning area was constant as the shape and size used as the propellant strand were the same. The area of the sample of the propellant strand is taken as 36 mm².

Table 4.18: Mass flow rate value for all the CSP samples used in this research study

CSP samples (Propellant density)	Mass flow rate, $\dot{m}$ (g/s) Pressure				
	1.0 atm	1.5 atm	2.0 atm	2.5 atm	3.0 atm
AP CSP ($\rho = 0.0046$)	0.64	0.69	0.75	0.83	0.88
KMnO ₄ /AP (20:80) CPS ($\rho = 0.0047$)	0.73	0.80	0.96	1.01	1.07
KMnO ₄ /AP (40:60) CSP ($\rho = 0.0049$)	0.84	0.97	1.13	1.29	1.32
KMnO ₄ /AP (60:40) CSP ($\rho = 0.0049$)	0.76	0.81	0.96	1.00	1.06
KMnO ₄ /AP (80:20) CSP ($\rho = 0.005$)	0.68	0.72	0.76	0.87	0.90

Based on Table 4.18, the higher the pressure, the higher the value of $\dot{m}$ for all the CSP samples. This is due to the increased burn rate of the propellant, which is directly influenced by pressure. In addition, Lang et al. (2006) claimed that higher pressure results in more rapid decomposition of the propellant, generating more gas in a shorter period, which also contributes to a higher $\dot{m}$. The sample of KMnO_4/AP (40:60) CSP observed the highest $\dot{m}$ the value produced, and a sample of AP CSP shows the lowest value at all pressure regimes. From the data results of $\dot{m}$, it will elucidate the effect of burn rate properties on the performance of the propellant in terms of $\dot{m}$ that will have a significant effect on the production of thrust.

4.8.4 Summary

The objective of this study was to find and identify the significant factors that mainly influence the burn rate behaviour of CSP samples and elucidate the burn rate value of AP CSP and KMnO_4 samples with different ratios at different pressure regimes. Results showed that all individual and interaction effects were significant at $P < 0.5$. CSP samples were very significantly affected by both pressures ($P < 0.000$) followed by interaction between both factors ($P < 0.3$) and KMnO_4 to AP ratio ($P < 0.5$). Thus, the burn rate behaviour of CSP samples was significantly and positively affected by pressure and KMnO_4 to AP ratio.

It was observed that the burn rate increases when the pressure increases at all the AP and KMnO_4 to AP ratio CSP samples. Sample with KMnO_4 to AP ratio of 40:60 recorded the highest burn rate value of 7.32 mm/s at 3 atm

pressure. KMnO_4/AP (80:20) sample resulted in the lowest burn rate value with value of 5.0 mm/s at 3.0 atm pressure. Both pressure and the KMnO_4 to AP ratio significantly affect the burn rate value for all the samples. The burn rate value of CSP samples increases as the pressure increases because of the kinetic reaction of the reactant molecules. As pressure increases, the density of the gases in the combustion zone also increases, enhancing the conductive and convective heat transfer to the propellant surface. This more efficient heat transfer raises the temperature at the burning surface, causing the propellant to decompose and burn more rapidly. Burn rate properties of CSP samples influence the performance of the solid rocket motor in terms of mass flow rate ($\dot{m}$) value. However, the $\dot{m}$ value is also influenced by the density and area of the propellant sample. From the calculation, a sample of KMnO_4/AP (40:60) CSP resulted in the highest value of $\dot{m}$ while sample of AP CSP showed the lowest at 3.0 atm pressure with values of 1.32 g/s and 0.88 g/s, respectively. As in the burn rate result, the AP CSP sample exhibited a higher burn rate value compared to KMnO_4/AP (80:20), but due to the higher density of sample KMnO_4/AP (80:20), the $\dot{m}$ value was higher than AP CSP. This mass flow rate is a crucial parameter because it will affect the thrust value in the solid rocket motor application. For solid rocket motor applications, the suggested KMnO_4/AP dual oxidiser system's scalability and long-term effects provide both potential and limitations. Although KMnO_4 improves combustion efficiency and burn rate, its potent oxidising properties make processing and storage difficult on a larger scale. Careful formulation is necessary to guarantee consistent mixing, compatibility with binder, and stability over time. To preserve performance and safety under prolonged storage circumstances,

long-term ageing effects such as hygroscopic degradation and possible chemical interactions between KMnO_4 and AP must be assessed.



CHAPTER 5

SUMMARY, CONCLUSION AND RECOMMENDATIONS FOR FUTURE

RESEARCH

5.1 Conclusion

The research results permit the following conclusions:

- I. Experimental designs centred on ammonium perchlorate (AP) based composite solid propellant (CSP) were successfully designed and fabricated, experimental work was conducted, and the results data was evaluated. All the experimental works referred to the literature to ensure the standards and specifications of the research work are followed and to achieve the relevancy of the result data. Besides, experiments were designed based on the design of the experiment matrix generated by the MINITAB software.
- II. Novel dual oxidiser KMnO_4/AP were successfully evaluated, including their characterisation, thermal properties, morphological structure, elemental composition, surface area adsorption, and crystallinity properties. Some of the characterisations of the novel KMnO_4/AP are as follows:
 - (a) Physical properties and morphological structure dual oxidiser KMnO_4/AP

The process of mixing using agate mortar does not change the physical characteristics of the AP and KMnO_4 . The size of both AP and KMnO_4 powder structures has been reduced due to the grinding and crushing process during mixing. With an increasing ratio of KMnO_4 to AP, the colour of the mixture changes to become darker.

Through a scanning electron microscope (SEM), AP particles were observed to start adhering to the KMnO_4 surface to create another structure with a different crystallinity, which resulted in a noticeably new structure. This indicates that the AP particles have mechanically adhered to the surface and edges of the KMnO_4 and reduced the AP agglomeration.

(b) Brunauer-Emmett-Teller (BET) and crystallinity properties dual oxidiser KMnO_4/AP

Sample of KMnO_4/AP with a ratio of 40:60 has the highest value of volume adsorption and desorption with a value of approximately 2.25 mmol/g at a pressure of 1.0 P/ P_0 followed by sample KMnO_4/AP (60:40), KMnO_4/AP (20:80), and KMnO_4/AP (80:20). This high in absorption and desorption indicate that this sample has a significant surface area and porosity because the material has many accessible surface sites where gas molecules can be adsorbed.

As the particle of AP and KMnO_4 size increases due to the crushing using agate mortar, the broadening tends to decrease, and the peaks become sharper. Besides, the new structure of KMnO_4/AP had fewer grain boundaries and defects than pure KMnO_4 and AP.

(c) Thermal properties of dual oxidiser KMnO_4/AP

The sample KMnO_4/AP (40:60) starts to decompose at the earliest temperature of 221.9 °C, which significantly affects the reduction of AP thermal decomposition temperature. Besides, when the KMnO_4 sample was present, both the low-temperature decomposition (LTD) and high-temperature decomposition (HTD) of AP were found to decrease. Sample KMnO_4/AP with a ratio of 40:60 exhibits the most effective catalytic effect by lowering the LTD decomposition peak followed by sample KMnO_4/AP (20:80), KMnO_4/AP (60:40), KMnO_4/AP (20:80), AP, and KMnO_4/AP (80:20). Besides, sample KMnO_4/AP (40:60) also resulted in the highest heat release (ΔH) with value of 1759.5 (J/g).

- III. KMnO_4/AP dual oxidiser in the CSP system were successfully fabricated, and their properties have been characterised and evaluated. Physical properties, morphological structure, elemental composition, thermal properties, and heat of combustion properties of the CSP with

KMnO₄/AP as dual oxidiser have been elucidated. Besides, the chlorine content as a combustion by-product of CSP has also been determined. The conclusion of each result is as follows:

(a) Physical properties and morphological structure of KMnO₄/AP-based CSP

In the presence of KMnO₄, the CSP became darker, and the surface of the samples also became rougher. Along with the increasing ratio of KMnO₄ to AP, the CSP samples continue to become darker, and at the ratio of 60:40 and 80:20, the particle of KMnO₄ can be seen at the surface of the sample. This dark colour comes from incorporating KMnO₄/AP as a dual oxidiser, and their composition is dominant.

Through SEM analysis, as the ratio of KMnO₄ to AP increases, the rod-like structure of KMnO₄ can be seen clearly. AP particles become smaller from approximately 100 µm to 50 µm, and the structure of KMnO₄ also becomes shorter. Increasing the ratio of KMnO₄ to AP makes the structure of KMnO₄ more visible, and the AP particle seems to disappear. With this, the solid structure of KMnO₄/AP dual oxidiser can be seen clearly with AP particles that tend to stick on the KMnO₄ surface. Moreover, with the maximum ratio of KMnO₄ to AP, the morphological structure of the sample observed

more ductile properties as the HTPB binder holds the maximum solid particles of KMnO_4/AP in this ratio.

(b) Thermal properties of KMnO_4/AP -based CSP

In the CSP system, a sample of KMnO_4/AP (40:60) CSP exhibits the best performance, resulting in lower temperatures when completing the combustion process. This sample has a lower HTD temperature from 392.10°C to 331.32°C from the pure AP CSP, which the LTD and HTD merged. Besides, the KMnO_4/AP (40:60) CSP also resulted in the highest heat release (ΔH) with a value of 3721.2 J/g compared to all samples.

Thus, dual oxidiser KMnO_4/AP with a ratio of 40:60 is the best formulation to boost the combustion performance of AP-based CSP systems.

(c) Heat of combustion of KMnO_4/AP -based CSP

The heat of combustion value decreases at the ratio of 60:60 and 80:20 with values of 1249.65 cal/g and 1247.73 cal/g , respectively. It is noticed that the highest value of heat of combustion is in the sample of KMnO_4/AP (40:60) CSP with a value of 1254.01 cal/g followed by sample KMnO_4/AP (20:80) CSP, KMnO_4/AP (60:40) CSP, KMnO_4/AP (80:20), and AP

CSP. Hence, this sample has the highest combustion efficiency percentage, with a value of 100.2 % compared to the other samples.

(d) Chlorine content of KMnO_4/AP -based CSP

The chlorine content reduction percentage is increasing with increasing ratio of KMnO_4 to AP. Sample of KMnO_4/AP with a ratio of 80:20 resulted in the highest chlorine content reduction from the pure AP CSP sample with a value of 58.25%. This reduction in chlorine content is due to the minimum use of AP in CSP formulation, which will produce HCl gases as a combustion by-product. Besides, this sample has been compared to other literature samples and found to have the highest percentage of chlorine content reduction.

IV. Statistical analysis was successfully conducted to determine the effect of individual factor and their interactions on the properties of the CSP on selected factors and validation data using RSM. The type of testing using RSM was done on mechanical and burn rate properties only. The results can be concluded as below:

(a) Tensile strength properties of AP and KMnO_4/AP -based CSP with various ratios.

The tensile strength of CSP samples was significantly and positively affected by both temperature and KMnO_4 to AP ratio. The CSP samples resulted in more ductile behaviour with increased temperature, and the lowest tensile strength can be achieved. Moreover, as the temperature increases, the tensile strength value of the samples decreases at all KMnO_4 to AP ratios. The maximum strain value of CSP samples increases as the temperature decreases, which can be attributed to the phase transition of the polymer binder. Besides, CSP samples observed the maximum Young's modulus value at the temperature of 0°C and KMnO_4 to AP ratio of 80:20 with a value of over 5.73 MPa. Thus, sample KMnO_4 (80:20) has the highest tensile strength to ensure they can withstand the mechanical loads and strains better during storage, transportation, and operation without cracking, fracturing, or deforming compared to others. The structural integrity of the propellant is vital for reliable performance and safety in various propulsion systems, such as rockets, missiles, and other applications.

(b) Burn rate of AP and KMnO_4 /AP-based CSP with various ratios.

The burn rate behaviour of CSP samples was significantly and positively affected by pressure and KMnO_4 to AP ratio. Sample with KMnO_4 to AP ratio of 40:60 CSP recorded the highest burn rate value of 7.32 mm/s at the 3.0 atm followed by KMnO_4 /AP (20:80) CSP, KMnO_4 /AP (60:40) CSP, AP CSP and KMnO_4 /AP (20:80) CSP. The

CSP burn rate performance of all samples has the same trend in all the pressure regimes. As pressure increases, the density of the gases in the combustion zone also increases, enhancing the conductive and convective heat transfer to the propellant surface. This more efficient heat transfer raises the temperature at the burning surface, causing the propellant to decompose and burn more rapidly. Besides, the burn rate properties greatly influence the solid rocket motor performance in terms of thrust produced. As the burn rate increases, the mass flow rate ($\dot{m}$) of the propellant sample increases, thus enhancing the thrust value produced by the solid rocket motor. Thus, from the calculated $\dot{m}$ value, KMnO_4/AP (40:60) resulted in the highest value of 1.32 g/s.

5.2 Main Contributions

CSP (40:60) sample was concluded and chosen as the most optimum as it improved the thermal decomposition temperature, resulted in 39.04% CI reduction, increased tensile strength value of nearly 2.5 MPa and recorded the highest burn rate with a value of 7.53 mm/s at 3 atm compared to conventional AP based CSP. This research is contradicted to make the following contributions in solid rocket propellant motor application, specifically on the development of environmentally friendly composite solid propellant (CSP). The research gives an overview of the current research and development progress in AP-based CSP, along with the relevant methodology and data analysis. Besides, the implementation of a superimposed contour plotting technique is used to determine the relationship between each significant factor on the CSP performance and properties. This research work

also gave a significant overview of the development of promising environmentally oxidiser for replacing the conventional AP oxidiser without compromising the performance in terms of thermal properties, HCl concentration as combustion by-product, tensile strength properties, and burn rate, as well as mass flow rate behaviour. Finally, the study formulated a novel composition of AP-based CSP that produces less toxic by-products in solid rocket motor applications.

5.3 Recommendation for future research

Several potential enhancements were identified during the investigation that could improve the development of environmentally friendly dual oxidisers. Firstly, the morphological structure of KMnO_4/AP can be studied with different KMnO_4 and AP particle sizes to illustrate the structure behaviour. Besides, different testing methods for detecting HCl or chlorine content in AP CSP combustion by-products can be done for data validation. Using other related methods or bigger setups for AP and KMnO_4 synthesis to fabricate a bigger sample size is also recommended to further the analysis from this research. Finally, further testing, such as ignition temperature testing, frictional sensitivity, and rocket motor static test, can be conducted for evaluation on practical application.

REFERENCES

- Abada, O., Abada, A., & El-Hirts, A. A. (2020). Effect of bipropellant combustion products on the rocket nozzle design. *Mechanics & Industry*, 21(5), 515.
- Abrishami, F., Zarei, A., & Karegar, M. (2018). Synthesis of novel plasticisers based on poly (ϵ -caprolactone) and considering their influence on nitroglycerine migration in double base solid propellants. *Central European Journal of Energetic Materials*, 15(1), 150-161.
- Adams, B. M., Bohnhoff, W. J., Dalbey, K. R., Ebeida, M. S., Eddy, J. P., Eldred, M. S., ... & Winokur, J. G. (2020). Dakota, a multilevel parallel object-oriented framework for design optimization, parameter estimation, uncertainty quantification, and sensitivity analysis: version 6.13 user's manual (No. SAND2020-12495). Sandia National Lab.(SNL-NM), Albuquerque, NM (United States).
- Adel, W. M., Kamal, H., & El-Soualeh, D. (2011, May). Experimental determination of some design properties of viscoelastic solid propellant using uniaxial tensile test. In *International Conference on Aerospace Sciences and Aviation Technology* (Vol. 14, No. AEROSPACE SCIENCES & AVIATION TECHNOLOGY, ASAT-14–May 24-26, 2011, pp. 1-11). The Military Technical College.
- Adeniyi, G. O., Nkere, I., Adetoro, L. M., & Sholiji, O. S. (2021). Performance Analysis of a Dual-Fuel Sugar Based Solid Rocket Propellant. *European Journal of Engineering and Technology Research*, 6(2), 34-41.
- Ahmed, T. L. A. E. S. I., Ali, A. A., El-Masry, A. M., & Tawfik, S. M. (2016). Development of Polyurethane-Based Solid Propellants Using Nanocomposite Materials. *Propellants, Explosives, Pyrotechnics*, 41(2), 286-294.
- Akbi, H., Rafai, S., Mekki, A., Toudjine, S., Fertassi, M., & Kadri, D. E. (2022). When Copper Oxide meets graphene oxide: A core-shell structure via an intermittent spray coating route for a highly efficient ammonium perchlorate thermal decomposition. *Journal of Organometallic Chemistry*, 957, 122159.
- Akhter, M. Z., & Hassan, M. A. (2020, February). Energetic Additives for Hybrid Rocket Propulsion-Review. In *2020 Advances in Science and Engineering Technology International Conferences (ASET)* (pp. 1-6). IEEE.
- Alamiery, A., Mahmoudi, E., & Allami, T. (2021). Corrosion inhibition of low-carbon steel in hydrochloric acid environment using a Schiff base derived from pyrrole: gravimetric and computational studies. *International Journal of Corrosion and Scale Inhibition*, 10(2), 749-765.

- Ali, H. M., El-Aal, M. A., Al-Hossainy, A. F., & Ibrahim, S. M. (2022). Kinetics and mechanism studies of oxidation of dibromothymolsulfonphthalein toxic dye by potassium permanganate in neutral media with the synthesis of 2-bromo-6-isopropyl-3-methyl-cyclohexa-2, 5-dienone. *ACS omega*, 7(18), 16109-16115.
- Altman, D. (2015). *Liquid propellant rockets* (Eds.). Princeton University Press.
- Álvarez-Hernández, M. H., Martínez-Hernández, G. B., Avalos-Belmontes, F., Castillo-Campohermoso, M. A., Contreras-Esquivel, J. C., & Artés-Hernández, F. (2019). Potassium permanganate-based ethylene scavengers for fresh horticultural produce as an active packaging. *Food Engineering Reviews*, 11, 159-183.
- An, E., Chen, S., Li, X., Tan, Y., Cao, X., & Deng, P. (2022). Thermal kinetics, thermodynamics, decomposition mechanism, and thermal safety performance of typical ammonium perchlorate-based molecular perovskite energetic materials. *Canadian Journal of Chemistry*, 100(5), 328-337.
- Antony, J. (2023). *Design of experiments for engineers and scientists*. Elsevier.
- Aprilliani, F., Warsiki, E., & Iskandar, A. (2018, March). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. In *IOP Conference Series: Earth and Environmental Science* (Vol. 141, p. 012003). IOP Publishing.
- Arkhipov, V. A., Zarko, V. E., Zharova, I. K., Zhukov, A. S., Kozlov, E. A., Aksenenko, D. D., & Kurbatov, A. V. (2016). Solid propellant combustion in a high-velocity cross-flow of gases. *Combustion, Explosion, and Shock Waves*, 52, 497-513.
- Asadollahzadeh, M., Niksirat, N., Tavakoli, H., Hemmati, A., Rahdari, P., Mohammadi, M., & Fazaeli, R. (2014). Application of multi-factorial experimental design to successfully model and optimize inorganic arsenic speciation in environmental water samples by ultrasound assisted emulsification of solidified floating organic drop microextraction. *Analytical methods*, 6(9), 2973-2981.
- Ashish, J., Swaroop, G., & Balasubramanian, K. (2019). Effect of ammonium perchlorate particle size on flow, ballistic, and mechanical properties of composite propellant. In *Nanomaterials in rocket propulsion systems* (pp. 299-362). Elsevier.
- Ashish, J., Swaroop, G., & Balasubramanian, K. (2019). Effect of ammonium perchlorate particle size on flow, ballistic, and mechanical properties of composite propellant. In *Nanomaterials in rocket propulsion systems* (pp. 299-362). Elsevier.

- Aziz, A., Mamat, R., & Ali, W. W. (2013, December). Development of strand burner for solid propellant burning rate studies. In IOP Conference Series: Materials Science and Engineering (Vol. 50, No. 1, p. 012048). IOP Publishing.
- Baxter, P., Aw, T. C., Cockcroft, A., Durrington, P., & Harrington, J. M. (Eds.). (2010). Hunter's diseases of occupations. CRC press.
- Becerra, M. E., Arias, N. P., Giraldo, O. H., Suárez, F. L., Gómez, M. I., & López, A. B. (2011). Soot combustion manganese catalysts prepared by thermal decomposition of KMnO_4 . *Applied Catalysis B: Environmental*, 102(1-2), 260-266.
- Beckstead, M. W. (1993). Solid propellant combustion mechanisms and flame structure. *Pure and applied chemistry*, 65(2), 297-307.
- Behera, S. K., Meena, H., Chakraborty, S., & Meikap, B. C. (2018). Application of response surface methodology (RSM) for optimization of leaching parameters for ash reduction from low-grade coal. *International Journal of Mining Science and Technology*, 28(4), 621-629.
- Bennewitz, J. W., Bigler, B. R., Hargus, W. A., Danczyk, S. A., & Smith, R. D. (2018). Characterization of detonation wave propagation in a rotating detonation rocket engine using direct high-speed imaging. In 2018 Joint Propulsion Conference (p. 4688).
- Betelin, V. B., Kushnirenko, A. G., Smirnov, N. N., Nikitin, V. F., Tyurenkova, V. V., & Stamov, L. I. (2018). Numerical investigations of hybrid rocket engines. *Acta Astronautica*, 144, 363-370.
- Bhowmik, D., Sadavarte, V. S., Charbhe, V. D., & Pande, S. M. (2017). Studies on sensitivity of nitrate ester plasticized hydroxyl terminated prepolymer based energetic solid rocket propellants. *Central European Journal of Energetic Materials*, 14(3).
- Bihari, B. K., Kumaraswamy, A., Jain, M., Rao, N. P., & Murthy, K. P. (2021). Effect of pressure on mechanical properties of composite propellant. *Propellants, Explosives, Pyrotechnics*, 46(5), 799-805.
- Biliaiev, M., Biliaieva, V., Kozachyna, V., Berlov, O., Gunko, O., & Chernyatyeva, K. (2019). Atmosphere pollution modeling in the case of accident during rocket propellant transportation by trains. In MATEC Web of Conferences (Vol. 294, p. 02003). EDP Sciences.
- Bommaraju, T. V. (2007). Salt, Chlor-Alkali, and Related Heavy Chemicals. In Kent and Riegel's Handbook of Industrial Chemistry and Biotechnology (pp. 1183-1214). Boston, MA: Springer US.

- Boshra, I. K., Lin, G., & Elbeih, A. (2021). Influence of different crosslinking mixtures on the mechanical properties of composite solid rocket propellants based on HTPB. *High Performance Polymers*, 33(1), 52-60.
- Boulangé, M., Lorgeoux, C., Biache, C., Saada, A., & Faure, P. (2019). Fenton-like and potassium permanganate oxidations of PAH-contaminated soils: Impact of oxidant doses on PAH and polar PAC (polycyclic aromatic compound) behavior. *Chemosphere*, 224, 437-444.
- Buturache, A. N. (2018). Performances study of a hybrid rocket engine. *INCAS Bulletin*, 10(2), 173-184.
- Cai, J., Deng, J., Yang, H., Tong, L., Wu, D., Wen, S., ... & Zhang, Y. (2020). A novel activation for ilmenite using potassium permanganate and its effect on flotation response. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 604, 125323.
- Casalino, L., Masseni, F., & Pastrone, D. (2018). Optimization of hybrid rocket engines for small satellite launchers. In *2018 Joint Propulsion Conference* (p. 4926).
- Cegla, M., Zmywaczyk, J., & Koniorczyk, P. (2019). Thermo-Mechanical Analysis of Heterogeneous Solid Rocket Propellant. *Issues of Armament Technology*, 147(3), 105-121.
- Cha, J. (2023). Numerical Simulation of Chemical Propulsion Systems: Survey and Fundamental Mathematical Modeling Approach. *Aerospace*, 10(10), 839.
- Chalghoum, F., Trache, D., Maggi, F., & Benziene, M. (2020). Effect of Complex Metal Hydrides on the Elimination of Hydrochloric Acid Exhaust Products from High-Performance Composite Solid Propellants: A Theoretical Analysis. *Propellants, Explosives, Pyrotechnics*, 45(8), 1204-1215.
- Chandru, R. A., Balasubramanian, N., Oommen, C., & Raghunandan, B. N. (2018). Additive manufacturing of solid rocket propellant grains. *Journal of Propulsion and Power*, 34(4), 1090-1093.
- Chaturvedi, S., & Dave, P. N. (2019). Solid propellants: AP/HTPB composite propellants. *Arabian Journal of Chemistry*, 12(8), 2061-2068.
- Chaudhary, A., Hussain, Z., Aihetasham, A., El-Sharnouby, M., Rehman, R. A., Khan, M. A. U., ... & Qamer, S. (2021). Pomegranate peels waste hydrolyzate optimization by Response Surface Methodology for Bioethanol production. *Saudi Journal of Biological Sciences*, 28(9), 4867-4875.
- Chen, F. Y., Xuan, C. L., Lu, Q. Q., Xiao, L., Yang, J. Q., Hu, Y. B., ... & Jiang, W. (2023). A review on the high energy oxidiser ammonium dinitramide:

- Its synthesis, thermal decomposition, hygroscopicity, and application in energetic materials. *Defence Technology*, 19, 163-195.
- Chen, S., Tang, Y., Zhang, W., Shen, R., Yu, H., Ye, Y., & DeLuca, L. T. (2019). Innovative methods to enhance the combustion properties of solid fuels for hybrid rocket propulsion. *Aerospace*, 6(4), 47.
- Chen, Y. S., & Wu, B. (2018). Development of a small launch vehicle with hybrid rocket propulsion. In *2018 Joint Propulsion Conference* (p. 4835).
- Chen, Y., Ma, K., Wang, J., Gao, Y., Zhu, X., & Zhang, W. (2018). Catalytic activities of two different morphological nano-MnO₂ on the thermal decomposition of ammonium perchlorate. *Materials Research Bulletin*, 101, 56-60.
- Chevillot, P. F., & Edwards, W. E. (1817). *Mémoire. Sur le caméléon mineral*. *Ann Chim Phys*, 4, 287-97.
- CHEVULA, S. (2019). Design and Testing of Rocket Motors with Composite Propellants. *Int. J. of Mechanical and Production Engineering Research and Development*, 9(4), 745-752.
- Collard, D. N., McClain, M., Fleck, T., Rahmann, N., Rhoads, J., Meyer, T., & Son, S. (2019). Solid propellant with embedded additively manufactured reactive components. In *AIAA Propulsion and Energy 2019 Forum* (p. 4443).
- Cui, P., Li, Q., Cheng, P., & Chen, L. (2020). System scheme design for LOX/LCH₄ variable thrust liquid rocket engines using motor pump. *Acta Astronautica*, 171, 139-150.
- Da Cunha, B. C. C., & Rocco, J. A. F. F. (2022). The influence of the type and size of the reactor and the influence of the heating interruption during curing on the solid composite propellant properties. *Journal of Applied Polymer Science*, 139(6), 51609.
- Dalinger, I. L., Suponitsky, K. Y., Shkineva, T. K., Lempert, D. B., & Sheremetev, A. B. (2018). Bipyrzole bearing ten nitro groups—a novel highly dense oxidiser for forward-looking rocket propulsions. *Journal of Materials Chemistry A*, 6(30), 14780-14786.
- Dallas, J. A., Raval, S., Gaitan, J. A., Saydam, S., & Dempster, A. G. (2020). The environmental impact of emissions from space launches: A comprehensive review. *Journal of Cleaner Production*, 255, 120209.
- Davenas, A. (Ed.). (2012). *Solid rocket propulsion technology*. Newnes.
- de Francqueville, F., Diani, J., Gilormini, P., & Vandenbroucke, A. (2021). Use of a micromechanical approach to understand the mechanical behavior of solid propellants. *Mechanics of Materials*, 153, 103656.

- de Iaco Veris, A., & de Iaco Veris, A. (2021). Fundamental Concepts on Liquid-Propellant Rocket Engines (pp. 1-61). Springer International Publishing.
- De Iaco Veris, A., & de Iaco Veris, A. (2021). Fundamental Concepts on Liquid-Propellant Rocket Engines (pp. 1-61). Springer International Publishing.
- DeLuca, L. T., Bohn, M. A., Gettwert, V., Weiser, V., & Tagliabue, C. (2018). Innovative solid rocket propellant formulations for space propulsion. In *Energetic Materials Research, Applications, and New Technologies* (pp. 1-24). IGI Global.
- Demko, A. R., Allen, T. W., Dillier, C., Sammet, T., Petersen, E. L., Reid, D. L., & Seal, S. (2018). Temperature sensitivity of composite propellants containing novel nano-additive catalysts. *Journal of Propulsion and Power*, 34(3), 795-807.
- Dey, A., Sikder, A. K., Talawar, M. B., & Chottopadhyay, S. (2015). Towards new directions in oxidisers/energetic fillers for composite propellants: an overview. *Central European Journal of Energetic Materials*, 12(2).
- Dinesh Kumar, B., Shishira Nayana, B., & Shravya Shree, D. (2016). Design and structural analysis of solid rocket motor casing hardware used in aerospace applications. *J Aeronaut Aerospace Eng*, 5(166), 2.
- Dîrloman, F. M., Rotariu, A. N., Rotariu, T., Noja, G. F., Ginghină, R. E., & Zvîncu, N. D. (2024). Ballistic and thermal characterisation of greener composite solid propellants based on phase stabilized ammonium nitrate. *Case Studies in Thermal Engineering*, 54, 103987.
- Doll, D. W., & Lund, G. K. (1992). Magnesium-neutralized propellant. *Journal of Propulsion and Power*, 8(6), 1185-1191.
- Dong, W. S., Cao, W. L., Wu, X. W., Hu, Y., Zhang, C., & Zhang, J. G. (2022). Energetic bimetallic complexes as catalysts affect the thermal decomposition of ammonium perchlorate. *Dalton Transactions*, 51(25), 9894-9904.
- Duan, B., Zhang, H., Hua, Z., Wu, L., Bao, Z., Guo, N., ... & Shen, R. (2022). Burning characteristics and combustion wave model of AP/AN-based laser-controlled solid propellant. *Energy*, 253, 124007.
- Ebrahimi, A., Khajavi, M. Z., Mortazavian, A. M., Asilian-Mahabadi, H., Rafiee, S., Farhoodi, M., & Ahmadi, S. (2021). Preparation of novel nano-based films impregnated by potassium permanganate as ethylene scavengers: an optimization study. *Polymer Testing*, 93, 106934.

- El-Sayed, S. A. (2022). Review of thermal decomposition, kinetics parameters and evolved gases during pyrolysis of energetic materials using different techniques. *Journal of Analytical and Applied Pyrolysis*, 161, 105364.
- Emelyanov, V. N., Teterina, I. V., & Volkov, K. N. (2020). Dynamics and combustion of single aluminium agglomerate in solid propellant environment. *Acta Astronautica*, 176, 682-694.
- Emrich Jr, W. J. (2023). *Principles of Nuclear Rocket Propulsion* (Eds.). Elsevier.
- Essel, J. T., Nelson, A. P., Smilowitz, L. B., Henson, B. F., Merriman, L. R., Turnbaugh, D., ... & Shermer, K. B. (2020). Investigating the effect of chemical ingredient modifications on the slow cook-off violence of ammonium perchlorate solid propellants on the laboratory scale. *Journal of Energetic Materials*, 38(2), 127-141.
- Farhadi Abkanar, F., Eslami, A., & Kubicki, M. (2020). Direct synthesis of Zn (II) and Cu (II) coordination polymers based on 4, 4'-bipyridine and 1, 10-phenanthroline and evaluating their effects as catalyst on ammonium perchlorate thermal decomposition. *Journal of Thermal Analysis and Calorimetry*, 140(4), 1779-1789.
- Farhadi Abkanar, F., Eslami, A., & Kubicki, M. (2020). Direct synthesis of Zn (II) and Cu (II) coordination polymers based on 4, 4'-bipyridine and 1, 10-phenanthroline and evaluating their effects as catalyst on ammonium perchlorate thermal decomposition. *Journal of Thermal Analysis and Calorimetry*, 140(4), 1779-1789.
- Farooq, U., Waqas, H., Imran, M., Alghamdi, M., & Muhammad, T. (2021). On melting heat transport and nanofluid in a nozzle of liquid rocket engine with entropy generation. *Journal of Materials Research and Technology*, 14, 3059-3069.
- Feodosiev, V. I., & Siniarev, G. B. (2014). *Introduction to rocket technology*. Academic Press.
- Fertassi, M. A., Belkhiri, S., Toudjine, S., Hamdane, A., Kechit, H., Boulkadid, M. K., & Khimeche, K. (2023). Enhancing the thermal decomposition of composite modified double base propellant using Al/hematite and Al/hematite/graphene thermites. *Reaction Kinetics, Mechanisms and Catalysis*, 136(6), 3127-3149.
- Frolov, S. M., Aksenov, V. S., Ivanov, V. S., Medvedev, S. N., Shamshin, I. O., Yakovlev, N. N., & Kostenko, I. I. (2018, February). Rocket engine with continuous detonation combustion of the natural gas–oxygen propellant system. In *Doklady physical chemistry* (Vol. 478, pp. 31-34). Pleiades Publishing.

- Fujimura, K., & Miyake, A. (2010). Effect of the particle size and specific surface area of ferric oxide catalyst on the burning rate of AP/HTPB solid propellant. *Sci Technol Energ Mater*, 71(3-4), 65-68.
- Gallier, S., Ferrand, A., & Plaud, M. (2016). Three-dimensional simulations of ignition of composite solid propellants. *Combustion and Flame*, 173, 2-15.
- Gallo, G., Mungiguerra, S., & Savino, R. (2021). New entrainment model for modelling the regression rate in hybrid rocket engines. *Journal of Propulsion and Power*, 37(6), 893-909.
- Gańczyk-Specjalska, K., Paziewska, P., Bogusz, R., Lewczuk, R., Cieślak, K., & Uszyński, M. (2021). Performance and Sensitivity Properties of Solid Heterogeneous Rocket Propellant Based on a Binary System of oxidisers (PSAN and AP). *Processes*, 9(12), 2201.
- Garino, S., Antonaci, P., Pastrone, D., Sangermano, M., & Maggi, F. (2021). Photo-polymerization for additive manufacturing of composite solid propellants. *Acta Astronautica*, 182, 58-65.
- Genevieve, B., Pitot de la Beaujardiere, J. F., & Brooks, M. J. (2017). A computational tool for predicting hybrid rocket motor performance. *R&D Journal*, 33, 56-65.
- Gieras, M., & Gorgeri, A. (2021). Numerical modelling of the hybrid rocket engine performance. *Propulsion and Power Research*, 10(1), 15-22.
- Gill, P. E., Murray, W., & Wright, M. H. (2021). Numerical linear algebra and optimization. Society for Industrial and Applied Mathematics.
- Glotov, O. G., Poryazov, V. A., Surodin, G. S., Sorokin, I. V., & Krainov, D. A. (2023). Combustion features of boron-based composite solid propellants. *Acta Astronautica*, 204, 11-24.
- Gnanaprakash, K., & Chakravarthy, S. R. (2018). Effect of curing agent on the plateau burning mechanism of solid propellant sandwiches. *Journal of Propulsion and Power*, 34(6), 1442-1454.
- GÖK, M. G., & CİHAN, Ö. (2020). Energetic materials and metal borides for solid propellant rocket engines. *The International Journal of Materials and Engineering Technology*, 3(2), 109-119.
- Gong, L., Li, Y., Guo, Y., Li, J., & Yang, R. (2020). Effect of Morphology for Ammonium Dinitramide on the Mechanical and Combustion Properties of Composite Propargyl-terminated Copolyether Propellant. *Propellants, Explosives, Pyrotechnics*, 45(6), 864-870.
- Gou, B., Kou, Y., Hu, Y., Zhang, G., Guo, H., Xiao, L., ... & Hao, G. (2022). Effect of Nano-Copper Chromite on the Thermal Decomposition and

Combustion of AP-Based Solid Propellants. *Propellants, Explosives, Pyrotechnics*, 47(10), e202200087.

Griego, C., Yilmaz, N., & Atmanli, A. (2019). Analysis of aluminum particle combustion in a downward burning solid rocket propellant. *Fuel*, 237, 405-412.

Hafizi, M., Mamat, R., Aziz, A. B., Noor, M. M., & Tamimi, A. (2017, February). Development of strand burner test by using aluminized AP/HTPB. In *Materials Science Forum* (Vol. 880, pp. 99-104). Trans Tech Publications Ltd.

Hamim, N., Aristiawan, Y., Hindayani, A., Andreas, A., & Komalasari, I. (2023, October). Method verification for determination of sodium chloride purity: A comparison of potentiometric and mohl titration. In *AIP Conference Proceedings* (Vol. 2902, No. 1). AIP Publishing.

Hargus, W. A., Schumaker, S. A., & Paulson, E. J. (2018). Air force research laboratory rotating detonation rocket engine development. In 2018 joint propulsion conference (p. 4876).

Heeg, F., Kilzer, L., Seitz, R., & Stoll, E. (2020). Design and test of a student hybrid rocket engine with an external carbon fiber composite structure. *Aerospace*, 7(5), 57.

Heister, S. D., Anderson, W. E., Pourpoint, T. L., Cassady, J., & Cassady, R. J. (2019). *Rocket propulsion* (Vol. 47). Cambridge University Press.

Hess, C. (2021). New advances in using Raman spectroscopy for the characterization of catalysts and catalytic reactions. *Chemical Society Reviews*, 50(5), 3519-3564.

Hinshelwood, C. N., & Bowen, E. J. (1921). The influence of physical conditions on the velocity of decomposition of certain crystalline solids. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 99(698), 203-212.

Hosseini, S. G., Gholami, S., & Mahyari, M. (2019). Superb catalytic properties of nickel cobalt bimetallic nanoparticles immobilized on 3D nitrogen-doped graphene for thermal decomposition of ammonium perchlorate. *Research on Chemical Intermediates*, 45, 1527-1543.

Hu, Y., Yang, Y., Lin, K., Hao, D., Qiu, L., Wang, D., ... & Xia, D. (2019). Ammonium perchlorate encapsulating nanothermites as high energetic composites: Preparation, thermal decomposition and combustion properties. *Chemical Engineering Science*, 207, 334-343.

Huggett, C., Bartley, C. E., & Mills, M. M. (Eds.) (2015). *Solid propellant rockets* (Vol. 2373). Princeton University Press.

- Ide, Y., Takahashi, T., Iwai, K., Nozoe, K., Habu, H., & Tokudome, S. (2015). Potential of ADN-based ionic liquid propellant for spacecraft propulsion. *Procedia Engineering*, 99, 332-337.
- Ilyushchenko, A. F., Letsko, A. I., Talako, T. L., Dyachkova, L. N., & Parnitsky, N. M. (2018). STRUCTURE AND PROPERTIES OF POWDERS FORMED IN Ni-Fe-Ti SYSTEMS WITH MECHANO-ACTIVATED SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS. *Bulletin PNRPU. Mechanical engineering, materials science*, 20(4), 78-87.
- Imiolek, A., Weiser, V., Locatelli, F., Tagliabue, C., Gettwert, V., & Bieroth, D. (2018). Burning behavior of ADN solid propellants in comparison to other oxidisers.
- Ismael, S., Deif, A., Maraden, A., Yehia, M., & Elbasuney, S. (2023). Ammonium perchlorate catalyzed with novel porous Mn-doped Co₃O₄ microspheres: superior catalytic activity, advanced decomposition kinetics and mechanisms. *Journal of Thermal Analysis and Calorimetry*, 148(21), 11811-11824.
- Jain, S., Chakraborty, S., & Qiao, L. (2019). Burn rate enhancement of ammonium perchlorate–nitrocellulose composite solid propellant using copper oxide–graphene foam micro-structures. *Combustion and Flame*, 206, 282-291.
- Ji, Y., Hu, W., Liao, J., Jiang, A., Xiu, Z., Gaowa, S., ... & Liu, C. (2020). Effect of atmospheric cold plasma treatment on antioxidant activities and reactive oxygen species production in postharvest blueberries during storage. *Journal of the Science of Food and Agriculture*, 100(15), 5586-5595.
- Jiang, C., Han, T., Gao, Z., & Lee, C. H. (2019). A review of impinging jets during rocket launching. *Progress in Aerospace Sciences*, 109, 100547.
- Jones, B. C. (1998). Suggestions for better referencing. *Journal of Business Communication*, 289(3): 42-45.
- Kadaganchi, R., Gankidi, M. R., & Gokhale, H. (2015). Optimization of process parameters of aluminum alloy AA 2014-T6 friction stir welds by response surface methodology. *Defence Technology*, 11(3), 209-219.
- Kalal, R. K., Jangid, S. K., Shekhar, H., Alegaonkar, P. S., & Kumar, A. (2020). Thermo-physical properties and combustion wave aspects of RDX contain low aluminium composite propellant. *Combustion and Flame*, 218, 12-17.
- Kanagarajan, B., Quinlan, J. M., & Runnels, B. (2022). A diffuse interface method for solid-phase modeling of regression behavior in solid composite propellants. *Combustion and Flame*, 242, 112219.

- Kashif, M., Jaafar, E., Bhadja, P., Low, F. W., Sahari, S. K., Hussain, S., ... & Al-Tamrah, S. A. (2021). Effect of potassium permanganate on morphological, structural and electro-optical properties of graphene oxide thin films. *Arabian Journal of Chemistry*, 14(2), 102953.
- Kaur, P., & Singh, K. (2020). Review of perovskite-structure related cathode materials for solid oxide fuel cells. *Ceramics International*, 46(5), 5521-5535.
- Kebritchi, A., & Taghi Nejad, H. M. (2018). Effect of Process Parameters on Pot Life of Solid Propellant Composite Based on Hydroxyl-Terminated Polybutadiene: A Short Review. *Basparesh*, 8(2), 52-62.
- Kechit, H., Belkhiri, S., Bhakta, A. K., Trache, D., Mekhalif, Z., & Tarchoun, A. F. (2021). The effect of iron decorated MWCNTs and iron-ionic liquid decorated MWCNTs onto thermal decomposition of ammonium perchlorate. *Zeitschrift für anorganische und allgemeine Chemie*, 647(16-17), 1607-1619.
- Keharom, S., Mahachai, R., & Chanthai, S. (2016). The optimization study of α -amylase activity based on central composite design-response surface methodology by dinitrosalicylic acid method. *International Food Research Journal*, 23(1).
- Keshtegar, B., & Heddami, S. (2018). Modeling daily dissolved oxygen concentration using modified response surface method and artificial neural network: a comparative study. *Neural Computing and Applications*, 30(10), 2995-3006.
- Khalil, M. M., Gomaa, A. M., Sebaei, A. S., & Moustapha, N. M. (2014). Distribution of phthalate esters in Egyptian edible oil. *Journal of Essential Oil Bearing Plants*, 17(6), 1343-1351.
- Khan, J. A., Khan, M. A., & Islam, R. (2012). Effect of potassium permanganate on mechanical, thermal and degradation characteristics of jute fabric-reinforced polypropylene composite. *Journal of Reinforced Plastics and Composites*, 31(24), 1725-1736.
- Khan, M. A. S., Vijayalakshmi, R., Singh, A., Nandi, A. K., & Talawar, M. B. (2019). Morphology of ammonium perchlorate in the presence of ethylene glycol as an additive: a first principle study. *CrystEngComm*, 21(48), 7519-7527.
- Khichar, M., Patidar, L., & Thynell, S. (2019). Comparative analysis of vaporization and thermal decomposition of cyclotrimethylenetrinitramine (RDX). *Journal of Propulsion and Power*, 35(6), 1098-1107.
- Khuri, A. I., & Cornell, J. A. (2018). *Response surfaces: designs and analyses*. CRC press.

- Kim, H. K., Kwak, H. D., Choi, C. H., & Kim, J. (2018). Conceptual Design of Electric-Pump Motor for 50kW Rocket Engine. *Journal of the Korean Society for Aeronautical & Space Sciences*, 46(2), 175-181.
- Kim, S. H., & Im, Y. T. (2019). Experimental study of material behavior of AP-HTPB base composite solid propellant. *Journal of Mechanical Science and Technology*, 33, 3355-3361.
- Kim, S. H., & Im, Y. T. (2019). Experimental study of material behavior of AP-HTPB base composite solid propellant. *Journal of Mechanical Science and Technology*, 33, 3355-3361.
- Kimura, T., Hashimoto, T., Sato, M., Takada, S., Moriya, S. I., Yagishita, T., ... & Ohmura, H. (2016). Reusable rocket engine: Firing tests and lifetime analysis of combustion chamber. *Journal of Propulsion and Power*, 32(5), 1087-1094.
- Kirby, L., Lawrence, A., Udaykumar, H. S., Sippel, T., & Song, X. (2023). Pressure-assisted binder jet additive manufacturing of solid propellants. *Additive manufacturing*, 77, 103808.
- Kleijnen, J. P. (2018). Design and analysis of simulation experiments (pp. 3-22). Springer International Publishing.
- Kline, D. J., Rehwoldt, M. C., Wang, H., Eckman, N. E., & Zachariah, M. R. (2019). Why does adding a poor thermal conductor increase propagation rate in solid propellants?. *Applied Physics Letters*, 115(11).
- Klinger, D., Casey, A., Manship, T., Son, S., & Strachan, A. (2023). Prediction of Solid Propellant Burning Rate Characteristics Using Machine Learning Techniques. *Propellants, Explosives, Pyrotechnics*, 48(4), e202200267.
- Kohga, M. (2019). Thermal Decomposition Behavior and Burning Characteristics of Ammonium Nitrate/Polytetrahydrofuran Propellants with Glycerol Propoxylate as a Crosslinking Agent. In *AIAA Propulsion and Energy 2019 Forum* (p. 4364).
- Kopacz, W., Okninski, A., Kasztankiewicz, A., Nowakowski, P., Rarata, G., & Maksimowski, P. (2022). Hydrogen peroxide—A promising oxidiser for rocket propulsion and its application in solid rocket propellants. *FirePhysChem*, 2(1), 56-66.
- Kosiba, G. D., Wixom, R. R., & Oehlschlaeger, M. A. (2017). High-Fidelity Microstructural Characterization and Performance Modeling of Aluminized Composite Propellant. *Propellants, Explosives, Pyrotechnics*, 42(12), 1387-1395.
- Kou, Y., Luo, P., Xiao, L., Xin, Y., Zhang, G., Hu, Y., ... & Hao, G. (2024). New insights in nano-copper chromite catalyzing ultrafine AP: Evaluation of dispersity and mixing uniformity. *Defence Technology*, 32, 120-133.

- Kuan, H., Lin, Z., Xinlong, C., & Chunwen, W. (2020, July). Optimal Calculation of Solid Propellant Burning Equilibrium Ingredients Based on Genetic Algorithm. In *Journal of Physics: Conference Series* (Vol. 1584, No. 1, p. 012026). IOP Publishing.
- Kumar, N., Patel, B. P., Rao, V. V., & Subhashchandran, B. S. (2019). Compressibility, damage, and age-hardening effects of solid propellants using finite strain constitutive model. *Journal of Engineering Materials and Technology*, 141(3), 031001.
- Kumar, P. (2018). An overview on properties, thermal decomposition, and combustion behavior of ADN and ADN based solid propellants. *Defence technology*, 14(6), 661-673.
- Kumar, P. (2018). An overview on properties, thermal decomposition, and combustion behavior of ADN and ADN based solid propellants. *Defence technology*, 14(6), 661-673.
- Kuzmin, V. A., Maratkanova, E. I., Zagray, I. A., & Rukavishnikova, R. V. (2015). Thermal radiation of heterogeneous combustion products in the model rocket engine plume. *Thermophysics and Aeromechanics*, 22, 371-386.
- Lang, A. J., & Vyazovkin, S. (2006). Effect of pressure and sample type on decomposition of ammonium perchlorate. *Combustion and flame*, 145(4), 779-790.
- Lawrence, A. R., Laktas, J. M., Place, G. J., Jelliss, P. A., Buckner, S. W., & Sippel, T. R. (2019). Organically-capped, nanoscale alkali metal hydride and aluminum particles as solid propellant additives. *Journal of Propulsion and Power*, 35(4), 736-746.
- Lee, D., & Lee, C. (2017). Hybrid gas generator for a staged hybrid rocket engine. *Journal of Propulsion and Power*, 33(1), 204-212.
- Lemos, M. F., & Bohn, M. A. (2018). DMA of polyester-based polyurethane elastomers for composite rocket propellants containing different energetic plasticizers. *Journal of Thermal Analysis and Calorimetry*, 131, 595-600.
- Li, D., Shao, Y., Ke, H., Chang, S., Kou, Y., Xiao, L., & Hao, G. (2023). Synthesis of Covalently Modified Energetic Graphene Oxide/CuO Composites with Enhanced Catalytic Performance for Thermal Decomposition of Ammonium Perchlorate. *ACS omega*, 8(25), 22876-22886.
- Li, H., Wang, S., Meng, L., Xu, J., Fan, X., & Chen, X. (2020). Experimental research on tensile mechanical properties of nepe propellant under confining pressure. *Propellants Explosives Pyrotechnics*, 45(11), 1769-1779.

- Li, T., Xu, J., Han, J., & He, Y. (2021). Effect of microstructure on micro-mechanical properties of composite solid propellant. *Micromachines*, 12(11), 1378.
- Lide, D. R. (Ed.). (2004). *CRC handbook of chemistry and physics* (Vol. 85). CRC press.
- Lin, G. (2018). Effect of bonding agent production materials on the mechanical properties of composite solid rocket propellant. In *MATEC Web of Conferences* (Vol. 189, p. 08001). EDP Sciences.
- Liu, L., Ao, W., Wen, Z., Zhang, Y., Lv, X., Qin, Z., & Liu, P. (2021). Combustion promotion and agglomeration reduction of the composite propellant using graphene. *Aerospace Science and Technology*, 118, 106988.
- Liu, Y., Hu, L. S., Gong, S., Guang, C., Li, L., Hu, S., & Deng, P. (2020). Study of ammonium perchlorate-based molecular perovskite (H₂DABCO)[NH₄(ClO₄)₃]/graphene energetic composite with insensitive performance. *Central European Journal of Energetic Materials*, 17(3), 451-469.
- Lysien, K., Stolarczyk, A., & Jarosz, T. (2021). Solid propellant formulations: A review of recent progress and utilized components. *Materials*, 14(21), 6657.
- Ma, S., Fan, H., Zhang, N., Li, W., Li, Y., Li, Y., ... & Xu, H. (2020). Investigation of a low-toxicity energetic binder for a solid propellant: curing, microstructures, and performance. *ACS omega*, 5(47), 30538-30548.
- Mahjub, A., Mazlan, N. M., Abdullah, M. Z., & Azam, Q. (2020). Design optimization of solid rocket propulsion: a survey of recent advancements. *Journal of Spacecraft and Rockets*, 57(1), 3-11.
- Manash, A., & Kumar, P. (2019). Comparison of burn rate and thermal decomposition of AP as oxidiser and PVC and HTPB as fuel binder based composite solid propellants. *Defence Technology*, 15(2), 227-232.
- Mao, X., Zhu, C., Li, Y., Li, Y., Jiang, L., & Wang, X. (2019). The Effect of Microsized Aluminum Powder on Thermal Decomposition of HNIW (CL-20). *Advances in Materials Science and Engineering*, 2019.
- Mason, B. P., & Roland, C. M. (2019). Solid propellants. *Rubber Chemistry and Technology*, 92(1), 1-24.
- Mazzetti, A., Merotto, L., & Pinarello, G. (2016). Paraffin-based hybrid rocket engines applications: A review and a market perspective. *Acta Astronautica*, 126, 286-297.
- McClain, M. S., Afriat, A., Montano, B. J., Rhoads, J. F., Gunduz, I. E., & Son, S. F. (2021). Dynamic combustion of functionally graded additively

- manufactured composite solid propellant. *Journal of Propulsion and Power*, 37(5), 725-732.
- Mehr, H. M., & Koocheki, A. (2020). Effect of atmospheric cold plasma on structure, interfacial and emulsifying properties of Grass pea (*Lathyrus sativus* L.) protein isolate. *Food Hydrocolloids*, 106, 105899.
- Micci, M. M. (Ed.). (2000). *Micropropulsion for small spacecraft* (Vol. 187). Aiaa.
- Milekhin, Y. M., Koptelov, A. A., Rogozina, A. A., & Shishov, N. I. (2019). Thermal Decomposition of Enegy Composite Material with an Inert Binder. *Russian Journal of Applied Chemistry*, 92(12), 1680-1689.
- Mishra, D. P. (Ed.) (2017). *Fundamentals of rocket propulsion*. CRC Press.
- Mucsi, G. (2019). A review on mechanical activation and mechanical alloying in stirred media mill. *Chemical Engineering Research and Design*, 148, 460-474.
- Mukherjee, S. (2022). Development of spinel magnesium aluminate by modified solid state process and its characterization. *Materials Today: Proceedings*, 67, 314-319.
- Mutrakulcharoen, P., Pornwongthong, P., Sahithi, S. A., Phusantisampan, T., Tawai, A., & Sriariyanun, M. (2021). Improvement of potassium permanganate pretreatment by enzymatic saccharification of rice straw for production of biofuels. In *E3S Web of Conferences* (Vol. 302, p. 02013). EDP Sciences.
- Nagendra, K., Ramakrishna, P. A., Sangtyani, R., & Kumar, A. (2023). Binder melt: Composite propellants with RDX. *Propellants, Explosives, Pyrotechnics*, 48(12), e202300171.
- Nair, S., Mathew, S., & Reghunadhan Nair, C. P. (2020). Lattice inclusion of copper ions in ammonium perchlorate through co-crystallization: impact on lattice, physical, and thermal characteristics. *ACS omega*, 5(30), 18544-18550.
- Najser, T., Gaze, B., Knutel, B., Verner, A., Najser, J., Mikeska, M., ... & Němček, O. (2022). Analysis of the effect of catalytic additives in the agricultural waste combustion process. *Materials*, 15(10), 3526.
- Nakka, R. (1997). *Richard Nakka's Experimental Rocketry Site*. Richard Nakka.
- Naseem, H., Murthy, H., & Ramakrishna, P. A. (2021). Accelerated ageing of composite solid propellants under cyclic temperature variations. *Journal of Energetic Materials*, 39(4), 452-478.

- Nosseir, A. E., Cervone, A., & Pasini, A. (2021). Review of state-of-the-art green monopropellants: For propulsion systems analysts and designers. *Aerospace*, 8(1), 20.
- Oluwoye, I., Altarawneh, M., Gore, J., & Dlugogorski, B. Z. (2020). Burning properties of redox crystals of ammonium nitrate and saccharides. *Combustion and Flame*, 213, 132-139.
- Oztan, C., & Coverstone, V. (2021). Utilization of additive manufacturing in hybrid rocket technology: A review. *Acta astronautica*, 180, 130-140.
- Pal, Y., Kumar, K. H., & Li, Y. H. (2019). Ballistic and mechanical characteristics of paraffin-based solid fuels. *CEAS Space Journal*, 11, 317-327.
- Pandey, P., & Pandey, M. M. (2021). Research methodology tools and techniques. Bridge Center.
- Pang, W. Q., Wang, K., Xu, H. X., Li, J. Q., Xiao, L. Q., Fan, X. Z., & Li, H. (2020). Combustion features of nitrate ester plasticized polyether solid propellants with ADN and Fox-12 particles. *International Journal of Energetic Materials and Chemical Propulsion*, 19(1).
- Papliński, A. S. (2019). Explosive potential of energetic mixtures based on hydrogen peroxide. *Materiały Wysokoenergetyczne*, 11(2).
- Park, S., Choi, S., Kim, K., Kim, W., & Park, J. (2020). Effects of ammonium perchlorate particle size, ratio, and total contents on the properties of a composite solid propellant. *Propellants, Explosives, Pyrotechnics*, 45(9), 1376-1381.
- Pauline, A. L., & Joseph, K. (2020). Hydrothermal carbonization of organic wastes to carbonaceous solid fuel—A review of mechanisms and process parameters. *Fuel*, 279, 118472.
- Pérez-Roca, S., Marzat, J., Piet-Lahanier, H., Langlois, N., Farago, F., Galeotta, M., & Le Gonidec, S. (2019). A survey of automatic control methods for liquid-propellant rocket engines. *Progress in Aerospace Sciences*, 107, 63-84.
- Pérez-Roca, S., Marzat, J., Piet-Lahanier, H., Langlois, N., Farago, F., Galeotta, M., & Le Gonidec, S. (2019). A survey of automatic control methods for liquid-propellant rocket engines. *Progress in Aerospace Sciences*, 107, 63-84.
- Petersen, E. D., Rodriguez, F. A., Thomas, J. C., Dillier, C. A., & Petersen, E. L. (2019). Combustion behavior of ammonium perchlorate at high pressures. In *AIAA Propulsion and Energy 2019 Forum* (p. 4366).

- Piezer, K., Li, L., Jeon, Y., Kadudula, A., & Seo, Y. (2021). The application of potassium permanganate to treat cyanobacteria-laden water: a review. *Process Safety and Environmental Protection*, 148, 400-414.
- Pimont, L. J., Fernandes, P. C. G., de Araujo Ferrão, L. F., Nagamachi, M. Y., & Cardoso, K. P. (2019). Study on the mechanical properties of solid composite propellant used as a gas generator. *Journal of Aerospace Technology and Management*, 11.
- Pinalia, A., Prianto, B., & Setyaningsih, H. (2021, September). Preliminary results of DOA plasticizer effect on AP/HTPB composite propellant characteristics. In *AIP Conference Proceedings* (Vol. 2366, No. 1). AIP Publishing.
- Polis, M., Szydło, K., Jarosz, T., Procek, M., Skóra, P., & Stolarczyk, A. (2022). Investigation of combustion of KMnO_4/Zn pyrotechnic delay composition. *Materials*, 15(18), 6406.
- Popov, P. P., Sirignano, W. A., & Sideris, A. (2015). Propellant injector influence on liquid-propellant rocket engine instability. *Journal of Propulsion and Power*, 31(1), 320-331.
- Pradhan, S. K., Kedia, V., & Kour, P. (2020). Review on different materials and their characterization as rocket propellant. *Materials Today: Proceedings*, 33, 5269-5272.
- Pye, H. O., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., ... & Zuend, A. (2020). The acidity of atmospheric particles and clouds. *Atmospheric chemistry and physics*, 20(8), 4809-4888.
- Pylypenko, O. V., Dolhopolov, S. I., Nikolayev, O. D., & Khorjak, N. V. (2020). Mathematical simulation of the start of a multiengine liquid-propellant rocket propulsion system. *Technical mechanics*, (1), 5-18.
- Rao, D. C. K., Yadav, N., & Joshi, P. C. (2016). Cu–Co–O nano-catalysts as a burn rate modifier for composite solid propellants. *Defence Technology*, 12(4), 297-304.
- Ren, J., Cao, J. P., Yang, F. L., Zhao, X. Y., Tang, W., Cui, X., ... & Wei, X. Y. (2019). Layered uniformly delocalized electronic structure of carbon supported Ni catalyst for catalytic reforming of toluene and biomass tar. *Energy conversion and management*, 183, 182-192.
- Rettinger, R. C. (2019). Examination of Non-Ideal Explosives.
- Rijesh, M., Sreekanth, M. S., Deepak, A., Dev, K., & Surendranathan, A. O. (2018). Effect of milling time on production of aluminium nanoparticle by high energy ball milling. *Int. J. Mech. Eng. Technol*, 9(8), 646-652.
- Ríos, P. L., Povea, P., Cerda-Cavieles, C., Arroyo, J. L., Morales-Verdejo, C., Abarca, G., & Camarada, M. B. (2019). Novel in situ synthesis of copper

nanoparticles supported on reduced graphene oxide and its application as a new catalyst for the decomposition of composite solid propellants. *RSC advances*, 9(15), 8480-8489.

Roslan, N. J., Jamal, S. H., Rashid, J. I. A., Norrrahim, M. N. F., Khim, O. K., & Yunus, W. M. Z. W. (2024). Response surface methodology for optimization of nitrocellulose preparation from nata de coco bacterial cellulose for propellant formulation. *Heliyon*.

Rosly, M. B., Jusoh, N., Othman, N., Rahman, H. A., Noah, N. F. M., & Sulaiman, R. N. R. (2019). Effect and optimization parameters of phenol removal in emulsion liquid membrane process via fractional-factorial design. *Chemical Engineering Research and Design*, 145, 268-278.

Ross, M., & VeddA, J. A. (2018). The policy and science of rocket emissions. Center for Space Policy and Strategy, The Aerospace Corporation, 2-10.

Roy, P., Mondal, A., & Barai, B. (2016). CFD analysis of rocket engine nozzle. *International Journal of Advanced Engineering Research and Science (IJAERS)*, 3(1), 39-46.

Rudorf, G. (1901). Über die Einwirkung der Hitze auf übermangansaures Kalium. *Zeitschrift für anorganische Chemie*, 27(1), 58-61.

Runtu, K. R., Setiani, W. S., & Utami, M. (2023). Application Energetic Materials for Solid Composite Propellant to Support Defense Rocket Development. *International Journal of Social Science Research and Review*, 6(1), 153-159.

Rusch, G. M., Garrett, R., Tobin, P., Falke, E., & Lu, P. Y. (2002). The development of acute exposure guideline levels for hazardous substances. *Drug and chemical toxicology*, 25(4), 339-348.

Said, K. A. M., & Amin, M. A. M. (2015). Overview on the response surface methodology (RSM) in extraction processes. *Journal of Applied Science & Process Engineering*, 2(1).

Sangtyani, R., Saha, H. S., Kumar, A., Kumar, A., Gupta, M., & Chavan, P. V. (2019). An alternative approach to improve burning rate characteristics and processing parameters of composite propellant. *Combustion and Flame*, 209, 357-362.

Schmierer, C., Kobald, M., Fischer, U., Tomilin, K., Petrarolo, A., & Hertel, F. (2019). Advancing europe's hybrid rocket engine technology with paraffin and LOX. In *Proceedings of the 8th European Conference for Aeronautics and Space Sciences*.

Schulze, M., & Sattelmayer, T. (2017). Linear stability assessment of a cryogenic rocket engine. *International Journal of Spray and Combustion Dynamics*, 9(4), 277-298.

- Sebacher, D. I., Bendura, R. J., & Wornom, D. E. (1980). Hydrochloric acid aerosol and gaseous hydrogen chloride partitioning in a cloud contaminated by solid rocket exhaust. *Atmospheric Environment* (1967), 14(5), 543-547.
- Sergienko, A. V., Popenko, E. M., Slyusarsky, K. V., Larionov, K. B., Dzidziguri, E. L., Kondratyeva, E. S., & Gromov, A. A. (2019). Burning characteristics of the HMX/CL-20/AP/polyvinyltetrazole binder/Al solid propellants loaded with nanometals. *Propellants, Explosives, Pyrotechnics*, 44(2), 217-223.
- Sharma, J. K., Srivastava, P., Singh, G., Akhtar, M. S., & Ameen, S. (2015). Catalytic thermal decomposition of ammonium perchlorate and combustion of composite solid propellants over green synthesized CuO nanoparticles. *Thermochimica Acta*, 614, 110-115.
- Shukla, M., Boddu, V. M., Steevens, J. A., Damavarapu, R., & Leszczynski, J. (2017). *Energetic Materials* (Vol. 482). Springer International Publishing.
- Simontacchi, P., Blasi, R., Edeline, E., Sagnier, S., Ravier, N., Espinosa-Ramos, A., ... & Altenhoefer, P. (2019, July). Prometheus: Precursor of new low-cost rocket engine family. In 8th European Conference for Aeronautics and Space Sciences, EUCASS2019-FP0743, Madrid, Spain.
- Sims, S., Fischer, S., & Tagliabue, C. (2022). ADN Solid propellants with high burning rates as booster material for hypersonic applications. *Propellants, Explosives, Pyrotechnics*, 47(7), e202200028.
- Sinditskii, V., Chernyi, A. N., Serushkin, V. V., & Filatov, S. A. (2015). Combustion behaviors and mechanism of AP-based compositions with nitroester binders. *International Journal of Energetic Materials and Chemical Propulsion*, 14(5).
- Singh, P., Abhash, A., Yadav, B. N., Shafeeq, M., Singh, I. B., & Mondal, D. P. (2019). Effect of milling time on powder characteristics and mechanical performance of Ti4wt% Al alloy. *Powder Technology*, 342, 275-287.
- Song, T., & Shen, L. (2018). Review of reactor for chemical looping combustion of solid fuels. *International Journal of Greenhouse Gas Control*, 76, 92-110.
- Sreejith, K., Prasad, S., Bagavathiappan, R., Prasanth, C., Jeenu, R., Murugan, J. P., ... & Eswaran, V. (2021). Design, development, static and flight tests of reverse flow multiple nozzle solid rocket motor with high burn rate propellant. *Current Science*, 116-121.
- Stavert, D. M., Archuleta, D. C., Behr, M. J., & Lehnert, B. E. (1991). Relative acute toxicities of hydrogen fluoride, hydrogen chloride, and hydrogen bromide in nose-and pseudo-mouth-breathing rats. *Fundamental and applied toxicology*, 16(4), 636-655.

- Stevens, B., Koenig, J. Q., Rebolledo, V., Hanley, Q. S., & Covert, D. S. (1992). Respiratory effects from the inhalation of hydrogen chloride in young adult asthmatics. *Journal of occupational medicine*, 923-929.
- Stewart, J. R., Phylaktou, H. N., Andrews, G. E., & Burns, A. D. (2021). Evaluation of CFD simulations of transient pool fire burning rates. *Journal of Loss Prevention in the Process Industries*, 71, 104495.
- Suksila, T. (2018). Experimental investigation of solid rocket motors for small sounding rockets. In *IOP Conference Series: Materials Science and Engineering* (Vol. 297, No. 1, p. 012009). IOP Publishing.
- Sutton, G. P., & Biblarz, O. (Eds.) (2016). *Rocket propulsion elements*. John Wiley & Sons.
- Svedin, J. D., Veum, K. S., Ransom, C. J., Kitchen, N. R., & Anderson, S. H. (2023). An identified agronomic interpretation for potassium permanganate oxidizable carbon. *Soil Science Society of America Journal*, 87(2), 291-308.
- Szala, M. (2020). Development trends in artillery ammunition propellants. *Materiały Wysokoenergetyczne*, 12(2), 5-16.
- Tagliabue, C., Weiser, V., Imiolek, A., Bohn, M. A., Heintz, T., & Gettwert, V. (2016, June). Burning behavior of AN/ADN propellants. In *47th International Annual Conference of ICT*, Paper (Vol. 36, p. 28).
- Taylor, T. S. (Ed.) (2017). *Introduction to rocket science and engineering*. CRC Press.
- Terry, B. C., Sippel, T. R., Pfeil, M. A., Gunduz, I. E., & Son, S. F. (2016). Removing hydrochloric acid exhaust products from high performance solid rocket propellant using aluminum-lithium alloy. *Journal of hazardous materials*, 317, 259-266.
- Thomas, J. C., Rodriguez, F. A., Sammet, T., Dillier, C. A., Petersen, E. D., & Petersen, E. L. (2019). Manufacturing and Burning of Composite AP/HTPB/AP Laminate Propellants. In *AIAA Propulsion and Energy 2019 Forum* (p. 4365).
- Tizón, J. M., & Román, A. (2017). A mass model for liquid propellant rocket engines. In *53rd AIAA/SAE/ASEE Joint Propulsion Conference* (p. 5010).
- Tola, C., & Nikbay, M. (2018). Solid rocket motor propellant optimization with coupled internal ballistic–structural interaction approach. *Journal of Spacecraft and Rockets*, 55(4), 936-947.
- Tola, C., & Nikbay, M. (2018). Solid rocket motor propellant optimization with coupled internal ballistic–structural interaction approach. *Journal of Spacecraft and Rockets*, 55(4), 936-947.

- Tolmachoff, E. D., Baldwin, L. C., Essel, J. T., Hedman, T. D., Kalman, S. E., & Kalman, J. (2022). Effects of select metal oxides on the onset, rate and extent of low temperature ammonium perchlorate decomposition. *Journal of Energetic Materials*, 40(4), 429-444.
- Trache, D., Klapötke, T. M., Maiz, L., Abd-Elghany, M., & DeLuca, L. T. (2017). Recent advances in new oxidisers for solid rocket propulsion. *Green Chemistry*, 19(20), 4711-4736.
- Trache, D., Maggi, F., Palmucci, I., & DeLuca, L. T. (2018). Thermal behavior and decomposition kinetics of composite solid propellants in the presence of amide burning rate suppressants. *Journal of Thermal Analysis and Calorimetry*, 132, 1601-1615.
- Trokhimovskiy, A., Fedorova, A. A., Olsen, K. S., Alday, J., Korablev, O., Montmessin, F., ... & Shakun, A. V. (2021). Isotopes of chlorine from HCl in the Martian atmosphere. *Astronomy & Astrophysics*, 651, A32.
- Tsuchiya, H., Togashi, R., & Kohga, M. (2023). Burning characteristics of ammonium nitrate propellant containing fine ammonium perchlorate— influence of porosity of ammonium perchlorate. *Propellants, Explosives, Pyrotechnics*, e202300027.
- Unger, C. C., Holler, M., Krumm, B., & Klapötke, T. M. (2020). Oxygen-rich bis (trinitroethyl esters): Suitable oxidisers as potential ammonium perchlorate replacements. *Energy & Fuels*, 34(12), 16469-16475.
- Unni, A. A., Kulkarni, R., Singh, C., Singh, V., Varshini, V. M. P., & Shanmugaraj, G. (2020, February). Effects of adding powdered metals with the solid propellants—A review. In *Journal of Physics: Conference Series* (Vol. 1473, No. 1, p. 012048). IOP Publishing.
- Urbano, A., Selle, L., Staffelbach, G., Cuenot, B., Schmitt, T., Ducruix, S., & Candel, S. (2016). Exploration of combustion instability triggering using large eddy simulation of a multiple injector liquid rocket engine. *Combustion and Flame*, 169, 129-140.
- Vara, J. A., Dave, P. N., & Ram, V. R. (2019). Nanomaterials as modifier for composite solid propellants. *Nano-Structures & Nano-Objects*, 20, 100372.
- Varghese, T. L. (Ed.) (2017). *The chemistry and technology of solid rocket propellants (a treatise on solid propellants)* (Vol. 1). Allied Publishers.
- Vellaisamy, U., & Biswas, S. (2020). Effect of metal additives on neutralization and characteristics of AP/HTPB solid propellants. *Combustion and Flame*, 221, 326-337.
- Vernacchia, M. T. (2017). *Development, modeling and testing of a slow-burning solid rocket propulsion system* (Doctoral dissertation,

Massachusetts Institute of Technology, Department of Aeronautics and Astronautics).

- Vernot, E. H., MacEwen, J. D., Haun, C. C., & Kinkead, E. R. (1977). Acute toxicity and skin corrosion data for some organic and inorganic compounds and aqueous solutions. *Toxicology and Applied Pharmacology*, 42(2), 417-423.
- Vijay, C., Raguvarun, K., Bharghav, K. V. S., Balasubramaniam, K., & Ramakrishna, P. A. (2019). Use of X-ray computed tomography for validation of random packs of composite solid propellants. *Propellants, Explosives, Pyrotechnics*, 44(7), 915-922.
- Vo, N. D., Jung, M. Y., Oh, D. H., Park, J. S., Moon, I., & Oh, M. (2018). Moving boundary modeling for solid propellant combustion. *Combustion and Flame*, 189, 12-23.
- WANG Zhe-jun, QIANG Hong-fu, WANG Guang. (2016). Review on the Mechanical Properties and Constitutive Models of Solid Propellants[J]. *Chinese Journal of Energetic Materials*, 24(4):403-416.
- Wang, H., Rehwoldt, M. C., Wang, X., Yang, Y., & Zachariah, M. R. (2019). On the promotion of high temperature AP decomposition with silica mesoparticles. *Combustion and Flame*, 200, 296-302.
- Wang, S., Ye, B., An, C., Wang, J., & Li, Q. (2019). Synergistic effects between Cu metal-organic framework (Cu-MOF) and carbon nanomaterials for the catalyzation of the thermal decomposition of ammonium perchlorate (AP). *Journal of Materials Science*, 54(6), 4928-4941.
- Wang, Z. J., Qiang, H. F., Wang, G., & Geng, B. (2018). Strength criterion of composite solid propellants under dynamic loading. *Defence Technology*, 14(5), 457-462.
- Wang, Z., Hu, Q., Wang, G., & Huang, Q. (2015). Tensile mechanical properties and constitutive model for htpb propellant at low temperature and high strain rate. *Journal of Applied Polymer Science*, 132(24).
- Wang, Z., Xue, Z. H., Meng, K. J., Zhang, X. X., & Yan, Q. L. (2022). Decomposition and combustion of HTPB-based composite propellants containing intercalated HMX crystals with desired high energy but low burn rate. *Fuel*, 321, 124067.
- Wen, X., Chen, K., Sang, C., Yuan, S., & Luo, Y. (2021). Applying modified hyperbranched polyester in hydroxyl-terminated polyether/ammonium perchlorate/aluminium/cyclotrimethylenetrinitramine (HTPE/AP/Al/RDX) composite solid propellant. *Polymer International*, 70(1), 123-134.
- Westerlund, S. (Ed.) (2015). Design of ablative insulator for solid rocket booster.

- Wibowo, H. B. (2018, November). Current solid propellant research and development in Indonesia and its future direction. In *Journal of Physics: Conference Series* (Vol. 1130, No. 1, p. 012027). IOP Publishing.
- Widiyastuti, W., Nurlilasari, P., Affandi, S., & Setiawan, H. (2018, September). Electrolysis synthesis of MnO₂ in acidic environment and its electrochemical performance for supercapacitor. In *Journal of Physics: Conference Series* (Vol. 1093, No. 1, p. 012021). IOP Publishing.
- Wohlschlager, J., DiPasquale, L. C., & Vernot, E. H. (1976). Toxicity of solid rocket motor exhaust: Effects of HCl, HF, and alumina on rodents. *J. Combust. Toxicol*, 3, 61-70.
- Wu, W., Wang, Y., Han, W., Wang, G., Zhang, M., & Wang, J. (2023). Experimental research on solid fuel pre-combustion rotating detonation engine. *Acta Astronautica*, 205, 258-266.
- Wu, Z., Qing, P., Guo, G., Shi, B., & Hu, Q. (2019). EFFECT OF POTASSIUM-PERMANGANATE MODIFICATION ON THE MICROSTRUCTURE AND ADSORPTION PROPERTY OF ACTIVATED CARBON. *Materials & Technologies/Materiali in Tehnologije*, 53(6).
- Xiao, L. Q., Fan, X. Z., Li, J. Z., Qin, Z., Fu, X. L., Pang, W. Q., & Wang, Y. (2020). Effect of Al content and particle size on the combustion of HMX-CMDB propellant. *Combustion and Flame*, 214, 80-89.
- Xu, F., Aravas, N., & Sofronis, P. (2008). Constitutive modeling of solid propellant materials with evolving microstructural damage. *Journal of the Mechanics and Physics of Solids*, 56(5), 2050-2073.
- Xu, S., Pang, A. M., Wang, Y., Pan, X. Z., Li, S. W., Li, H. T., & Kong, J. (2022). A review on the use of burning rate suppressants in AP-based composite propellants. *Propellants, Explosives, Pyrotechnics*, 47(1), e202000327.
- Yadav, N., Srivastava, P. K., & Varma, M. (2021). Recent advances in catalytic combustion of AP-based composite solid propellants. *Defence Technology*, 17(3), 1013-1031.
- Yan, N., Qin, L., Li, J., Zhao, F., & Feng, H. (2018). Atomic layer deposition of iron oxide on reduced graphene oxide and its catalytic activity in the thermal decomposition of ammonium perchlorate. *Applied Surface Science*, 451, 155-161.
- Yan, X., Xia, Z., Huang, L., & Na, X. D. (2020). Combustion of nitrate ester plasticized polyether propellants. *Journal of Zhejiang University Science A*, 21(10), 834-847.
- Yang, W., Liu, W., Zheng, M., Zhang, X., Jin, P., Li, T., & Luo, Y. (2023). Preparation of PDA@AP composite particles by two-step method and its application in glycidyl azide polymer-energetic thermoplastic elastomer propellants. *Journal of Applied Polymer Science*, 140(45), e54654.

- Yang, Y., Zhu, T., Yan, Z., Li, Q., Liu, B., Wang, J., & Huang, Z. (2023). A Study on Combustion Characteristics of Insensitive Triple-Base Propellant. *Applied Sciences*, 13(9), 5462.
- Yeh, I. C., & Andzelm, J. W. (2021). Computational study of structural and energetic properties of ammonium perchlorate at interfaces. *The Journal of Physical Chemistry C*, 125(22), 12297-12304.
- Yildiz, M. S., Kokal, U., & Celik, M. (2017). Preliminary Thrust Measurement Results of the BUSTLab Microwave Electrothermal Thruster. In 53rd AIAA/SAE/ASEE Joint Propulsion Conference (p. 4725).
- Yogeshkumar, V., Rathi, N., & Ramakrishna, P. A. (2020). Solid Fuel-rich Propellant Development for use in a Ramjet to Propel an Artillery Shell. *Defence Science Journal*, 70(3).
- Yuan, J., Liu, J., Zhou, Y., Zhang, Y., & Cen, K. (2021). Thermal decomposition and combustion characteristics of Al/AP/HTPB propellant. *Journal of Thermal Analysis and Calorimetry*, 143, 3935-3944.
- Yuan, S., Jiang, S., & Luo, Y. (2021). Cross-linking network structures and mechanical properties of novel HTPE/PCL binder for solid propellant. *Polymer Bulletin*, 78, 313-334.
- Yudha, C. S., Hutama, A. P., Rahmawati, M., Widiyandari, H., Nursukatmo, H., Nilasary, H., ... & Purwanto, A. (2021). Synthesis and characterization of ZnO from thermal decomposition of precipitated zinc oxalate dihydrate as an anode material of li-ion batteries. *Energies*, 14(18), 5980.
- Zamostianu, A., & Yavor, Y. (2022). Burn rate of a novel boron-AN-water green solid propellant. *FirePhysChem*, 2(1), 76-82.
- Zeng, Z., & Bernstein, E. R. (2019). Ammonium perchlorate and ammonium dihydrogen phosphate as energetic materials: comparison to ammonium nitrate. *The Journal of Physical Chemistry C*, 123(19), 12149-12153.
- Zeping, W., Donghui, W., Weihua, Z., Okolo, N. P., & Yang, F. (2017). Solid-rocket-motor performance-matching design framework. *Journal of Spacecraft and Rockets*, 54(3), 698-707.
- Zhai, X., Jing, F., Li, L., Jiang, X., Zhang, J., Ma, J., & Chu, W. (2021). Toluene catalytic oxidation over the layered MOx- δ -MnO₂ (M= Pt, Ir, Ag) composites originated from the facile self-driving combustion method. *Fuel*, 283, 118888.
- Zhang, L. N., Lin, Q. Q., Cheng, B. D., Wang, P. C., Lu, M., & Lin, Q. H. (2021). Effect of hexanitroethane (HNE) and hydrazinium nitroformate (HNF) on energy characteristics of composite solid propellants. *FirePhysChem*, 1(2), 116-122.

Zhang, L., Zhi, S., & Shen, Z. (2018). Research on tensile mechanical properties and damage mechanism of composite solid propellants. *Propellants, Explosives, Pyrotechnics*, 43(3), 234-240.

Zhang, P., Tan, W., Zhang, X., Chen, J., Yuan, J., & Deng, J. (2021). Chemical modification of hydroxyl-terminated polybutadiene and its application in composite propellants. *Industrial & Engineering Chemistry Research*, 60(10), 3819-3829.

Zhang, Y., Zhao, Z., Xing, D., Hu, J., Liu, W., Wang, X., & Yao, L. (2024). Effect of inorganic salts/lignin on the combustion performance of torrefied biochar. *Energy*, 130707.

Zhou, S., Zhou, X., Tang, G., Guo, X., & Pang, A. (2020). Differences of thermal decomposition behaviors and combustion properties between CL-20-based propellants and HMX-based solid propellants. *Journal of Thermal Analysis and Calorimetry*, 140(5), 2529-2540.

Zumbo, A., Stumpo, L., Antonaci, P., Ferrero, A., Masseni, F., Polizzi, G., ... & Pastrone, D. (2024). Rheological and Mechanical Characterization of 3D-Printable Solid Propellant Slurry. *Polymers*, 16(5), 576.

APPENDICES

Appendix A1 (Uniaxial tensile test - FD)

RunOrder	Sample	Temperature C (V ₁)	Ratio KMnO ₄ to AP (V ₂)
1	S1	45	0
2	S2	35	40
3	S3	50	20
4	S4	45	40
5	S5	45	40
6	S6	45	40
7	S7	45	40
8	S8	45	80
9	S9	40	20
10	S10	45	40
11	S11	50	20
12	S12	40	20
13	S13	40	60
14	S14	40	60
15	S15	45	40
16	S16	35	40
17	S17	55	40
18	S18	45	40
19	S19	50	60
20	S20	55	40
21	S21	55	40
22	S22	45	40
23	S23	45	80
24	S24	45	40
25	S25	50	20
26	S26	45	40
27	S27	45	40
28	S28	40	20
29	S29	45	40

30	S30	45	0
31	S31	35	40
32	S32	40	60
33	S33	45	40
34	S34	45	40
35	S35	45	40
36	S36	45	80
37	S37	45	0
38	S38	50	60
39	S39	50	60

Appendix A2
(Burn rate test - FD)

RunOrder	Sample	Pressure (atm) (V ₁)	Ratio KMnO ₄ to AP (V ₂)
1	S1	2.5	60
2	S2	2	40
3	S3	1.5	60
4	S4	2	40
5	S5	2	0
6	S6	2	0
7	S7	2	40
8	S8	2.5	60
9	S9	3	40
10	S10	1	40
11	S11	3	40
12	S12	2	40
13	S13	2	40
14	S14	1.5	20
15	S15	2.5	20
16	S16	1.5	60
17	S17	2.5	20
18	S18	2	40
19	S19	2.5	60
20	S20	2	40
21	S21	2	0
22	S22	2	40
23	S23	2	40
24	S24	2	40
25	S25	2	40
26	S26	2	40
27	S27	1	40
28	S28	1.5	20
29	S29	2	40
30	S30	1	40
31	S31	2	80

32	S32	2	80
33	S33	1.5	60
34	S34	1.5	20
35	S35	2	40
36	S36	2.5	20
37	S37	2	80
38	S38	2	40
39	S39	3	40



Appendix A3
(Uniaxial tensile test - RSM)

Run Order	Sample	Coded factor		Uncoded factor	
		Temperature C (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Temperature C (V ₁)	Ratio KMnO ₄ to AP (V ₂)
1	S1	-1	1	45	0
2	S2	-1	1	35	40
3	S3	1	1	50	20
4	S4	0	1	45	40
5	S5	0	1	45	40
6	S6	0	1	45	40
7	S7	0	1	45	40
8	S8	-1	1	45	80
9	S9	1	1	40	20
10	S10	0	1	45	40
11	S11	1	1	50	20
12	S12	1	1	40	20
13	S13	1	1	40	60
14	S14	1	1	40	60
15	S15	0	1	45	40
16	S16	-1	1	35	40
17	S17	-1	1	55	40
18	S18	0	1	45	40
19	S19	1	1	50	60
20	S20	-1	1	55	40
21	S21	-1	1	55	40
22	S22	0	1	45	40
23	S23	-1	1	45	80
24	S24	0	1	45	40
25	S25	1	1	50	20
26	S26	0	1	45	40
27	S27	0	1	45	40
28	S28	1	1	40	20
29	S29	0	1	45	40

30	S30	-1	1	45	0
31	S31	-1	1	35	40
32	S32	1	1	40	60
33	S33	0	1	45	40
34	S34	0	1	45	40
35	S35	0	1	45	40
36	S36	-1	1	45	80
37	S37	-1	1	45	0
38	S38	1	1	50	60
39	S39	1	1	50	60

Appendix A4
(Burn rate test – RSM)

Run Order	Sample	Coded factor		Uncoded factor	
		Pressure (atm) (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Pressure (atm) (V ₁)	Ratio KMnO ₄ to AP (V ₂)
1	S1	1	1	2.5	60
2	S2	0	1	2	40
3	S3	1	1	1.5	60
4	S4	0	1	2	40
5	S5	-1	1	2	0
6	S6	-1	1	2	0
7	S7	0	1	2	40
8	S8	1	1	2.5	60
9	S9	-1	1	3	40
10	S10	-1	1	1	40
11	S11	-1	1	3	40
12	S12	0	1	2	40
13	S13	0	1	2	40
14	S14	1	1	1.5	20
15	S15	1	1	2.5	20
16	S16	1	1	1.5	60
17	S17	1	1	2.5	20
18	S18	0	1	2	40
19	S19	1	1	2.5	60
20	S20	0	1	2	40
21	S21	-1	1	2	0
22	S22	0	1	2	40
23	S23	0	1	2	40
24	S24	0	1	2	40
25	S25	0	1	2	40
26	S26	0	1	2	40
27	S27	-1	1	1	40
28	S28	1	1	1.5	20
29	S29	0	1	2	40

30	S30	-1	1	1	40
31	S31	-1	1	2	80
32	S32	-1	1	2	80
33	S33	1	1	1.5	60
34	S34	1	1	1.5	20
35	S35	0	1	2	40
36	S36	1	1	2.5	20
37	S37	-1	1	2	80
38	S38	0	1	2	40
39	S39	-1	1	3	40

Appendix B1
Heat of combustion (Combustion efficiency calculation)

$$\text{Combustion efficiency (\%)} = \text{Heat output} / \text{Heat input} \times 100$$

Heat output = Actual heat release during experiment

Heat input = Theoretical maximum heat released = 1251 cal/g

I. AP CSP

$$\text{Combustion efficiency (\%)} = \frac{1247}{1251} \times 100$$

$$\text{Combustion efficiency (\%)} = 99.7\%$$

II. KMnO₄/AP (20:80) CSP:

$$\text{Combustion efficiency (\%)} = \frac{1250.98}{1251} \times 100$$

$$\text{Combustion efficiency (\%)} = 99.9\%$$

III. KMnO₄/AP (40:60) CSP:

$$\text{Combustion efficiency (\%)} = \frac{1254.01}{1251} \times 100$$

$$\text{Combustion efficiency (\%)} = 100.2\%$$

IV. KMnO₄/AP (60:40) CSP:

$$\text{Combustion efficiency (\%)} = \frac{1249.65}{1251} \times 100$$

$$\text{Combustion efficiency (\%)} = 99.8\%$$

V. KMnO_4/AP (80:20) CSP:

$$\text{Combustion efficiency (\%)} = \frac{1247.73}{1251} \times 100$$

$$\text{Combustion efficiency (\%)} = 99.6\%$$



Appendix B2
HCl reduction test (Chlorine content calculation)

$M1$ = Molarity of AgNO_3 = 0.1

$V1$ = Volume of AgNO_3 used in dropper pipette

$M2$ = Molarity of water sample

$V2$ = Volume of the water sample = 10 ml

I. AP CSP:

Molarity of the water sample:

$$M1V1 = M2V2$$

$$(0.1 \text{ molar}) (2.1 \text{ ml}) = (M2) (10 \text{ ml})$$

$$M2 = \frac{(0.1 \text{ molar}) (2.1 \text{ ml})}{10 \text{ ml}}$$

$$M2 = 0.021$$

Strength of chloride (Cl^-) ion:

$$= M2 \times 35.5$$

$$= 0.021 \times 35.5$$

$$= 0.7455$$

Chlorine content in (ppm)

$$= \text{Strength of } \text{Cl}^- \text{ ion} \times 1000$$

$$= 0.7455 \times 1000$$

$$= 745.5 \text{ ppm}$$

II. KMnO_4/AP (20:80) CSP:

Molarity of the water sample:

$$M_1V_1 = M_2V_2$$

$$(0.1 \text{ molar}) (1.93 \text{ ml}) = (M_2) (10 \text{ ml})$$

$$M_2 = \frac{(0.1 \text{ molar}) (1.93 \text{ ml})}{10 \text{ ml}}$$

$$M_2 = 0.0193$$

Strength of chloride (Cl^-) ion:

$$= M_2 \times 35.5$$

$$= 0.0193 \times 35.5$$

$$= 0.685$$

Chlorine content in (ppm)

$$= \text{Strength of } \text{Cl}^- \text{ ion} \times 1000$$

$$= 0.685 \times 1000$$

$$= 685.15 \text{ ppm}$$

III. KMnO_4/AP (40:60) CSP:

Molarity of the water sample:

$$M_1V_1 = M_2V_2$$

$$(0.1 \text{ molar}) (1.28 \text{ ml}) = (M_2) (10 \text{ ml})$$

$$M_2 = \frac{(0.1 \text{ molar}) (1.28 \text{ ml})}{10 \text{ ml}}$$

$$M_2 = 0.0128$$

Strength of chloride (Cl^-) ion:

$$= M_2 \times 35.5$$

$$= 0.0128 \times 35.5$$

$$= 0.454$$

Chlorine content in (ppm)

$$= \text{Strength of } Cl^- \text{ ion} \times 1000$$

$$= 0.454 \times 1000$$

$$= 454.41 \text{ ppm}$$

IV. $KMnO_4/AP$ (60:40) CSP:

Molarity of the water sample:

$$M_1V_1 = M_2V_2$$

$$(0.1 \text{ molar}) (1.10 \text{ ml}) = (M_2) (10 \text{ ml})$$

$$M_2 = \frac{(0.1 \text{ molar}) (1.10 \text{ ml})}{10 \text{ ml}}$$

$$M_2 = 0.011$$

Strength of chloride (Cl^-) ion:

$$= M_2 \times 35.5$$

$$= 0.011 \times 35.5$$

$$= 0.39$$

Chlorine content in (ppm)

$$= \text{Strength of } Cl^- \text{ ion} \times 1000$$

$$= 0.39 \times 1000$$

$$= 390.54 \text{ ppm}$$

V. KMnO_4/AP (80:20) CSP:

Molarity of the water sample:

$$M_1V_1 = M_2V_2$$

$$(0.1 \text{ molar}) (0.87 \text{ ml}) = (M_2) (10 \text{ ml})$$

$$M_2 = \frac{(0.1 \text{ molar}) (0.87 \text{ ml})}{10 \text{ ml}}$$

$$M_2 = 0.0087$$

Strength of chloride (Cl^-) ion:

$$= M_2 \times 35.5$$

$$= 0.0087 \times 35.5$$

$$= 0.31$$

Chlorine content in (ppm)

$$= \text{Strength of } \text{Cl}^- \text{ ion} \times 1000$$

$$= 0.31 \times 1000$$

$$= 308.85 \text{ ppm}$$

Appendix B3
(Uniaxial tensile test - RSM result data)

I. Tensile strength

RunOrder	Sample	Coded factor		Uncoded factor		Responses
		Temperature °C (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Temperature °C (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Tensile strength (MPa)
1	S1	-1	1	45	0	0.6
2	S2	-1	1	35	40	1.5
3	S3	1	1	50	20	0.4
4	S4	0	1	45	40	0.85
5	S5	0	1	45	40	0.86
6	S6	0	1	45	40	0.75
7	S7	0	1	45	40	0.81
8	S8	-1	1	45	80	1.01
9	S9	1	1	40	20	0.9
10	S10	0	1	45	40	0.85
11	S11	1	1	50	20	0.4
12	S12	1	1	40	20	0.98
13	S13	1	1	40	60	1.21
14	S14	1	1	40	60	1.22
15	S15	0	1	45	40	0.85
16	S16	-1	1	35	40	1.55
17	S17	-1	1	55	40	0.23
18	S18	0	1	45	40	0.85
19	S19	1	1	50	60	0.6
20	S20	-1	1	55	40	0.21
21	S21	-1	1	55	40	0.2
22	S22	0	1	45	40	0.85
23	S23	-1	1	45	80	1.02
24	S24	0	1	45	40	0.84
25	S25	1	1	50	20	0.4
26	S26	0	1	45	40	0.85

27	S27	0	1	45	40	0.84
28	S28	1	1	40	20	0.99
29	S29	0	1	45	40	0.84
30	S30	-1	1	45	0	0.6
31	S31	-1	1	35	40	1.45
32	S32	1	1	40	60	1.21
33	S33	0	1	45	40	0.85
34	S34	0	1	45	40	0.84
35	S35	0	1	45	40	0.85
36	S36	-1	1	45	80	1.01
37	S37	-1	1	45	0	0.6
38	S38	1	1	50	60	0.65
39	S39	1	1	50	60	0.67

II. Maximum strain

RunOrder	Sample	Coded factor		Uncoded factor		Responses
		Temperature C (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Temperature C (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Maximum strain
1	S1	-1	1	45	0	3.85
2	S2	-1	1	35	40	3.65
3	S3	1	1	50	20	2.99
4	S4	0	1	45	40	3.63
5	S5	0	1	45	40	3.61
6	S6	0	1	45	40	3.62
7	S7	0	1	45	40	3.6
8	S8	-1	1	45	80	3.11
9	S9	1	1	40	20	3.84
10	S10	0	1	45	40	3.6
11	S11	1	1	50	20	2.99
12	S12	1	1	40	20	2.98
13	S13	1	1	40	60	3.27
14	S14	1	1	40	60	3.25

15	S15	0	1	45	40	3.63
16	S16	-1	1	35	40	3.66
17	S17	-1	1	55	40	2.8
18	S18	0	1	45	40	3.64
19	S19	1	1	50	60	2.59
20	S20	-1	1	55	40	2.75
21	S21	-1	1	55	40	2.78
22	S22	0	1	45	40	3.6
23	S23	-1	1	45	80	3.1
24	S24	0	1	45	40	3.62
25	S25	1	1	50	20	2.99
26	S26	0	1	45	40	3.6
27	S27	0	1	45	40	3.61
28	S28	1	1	40	20	3.83
29	S29	0	1	45	40	3.6
30	S30	-1	1	45	0	3.8
31	S31	-1	1	35	40	3.66
32	S32	1	1	40	60	3.27
33	S33	0	1	45	40	3.63
34	S34	0	1	45	40	3.62
35	S35	0	1	45	40	3.63
36	S36	-1	1	45	80	3.29
37	S37	-1	1	45	0	3.79
38	S38	1	1	50	60	2.6
39	S39	1	1	50	60	2.58

III. Young's modulus

RunOrder	Sample	Coded factor		Uncoded factor		Responses
		Temperature C (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Temperature C (V ₁)	Ratio KMnO ₄ to AP (V ₂)	
1	S1	-1	1	45	0	3.42
2	S2	-1	1	35	40	5.23
3	S3	1	1	50	20	3.32
4	S4	0	1	45	40	4.69
5	S5	0	1	45	40	4.7
6	S6	0	1	45	40	4.71
7	S7	0	1	45	40	4.72
8	S8	-1	1	45	80	5.19
9	S9	1	1	40	20	3.84
10	S10	0	1	45	40	4.7
11	S11	1	1	50	20	3.32
12	S12	1	1	40	20	3.84
13	S13	1	1	40	60	4.99
14	S14	1	1	40	60	4.98
15	S15	0	1	45	40	4.75
16	S16	-1	1	35	40	5.25
17	S17	-1	1	55	40	4.17
18	S18	0	1	45	40	4.63
19	S19	1	1	50	60	4.23
20	S20	-1	1	55	40	4.17
21	S21	-1	1	55	40	4.32
22	S22	0	1	45	40	4.76
23	S23	-1	1	45	80	5.29
24	S24	0	1	45	40	4.8
25	S25	1	1	50	20	3.32
26	S26	0	1	45	40	4.69
27	S27	0	1	45	40	4.72
28	S28	1	1	40	20	3.84

29	S29	0	1	45	40	4.71
30	S30	-1	1	45	0	3.43
31	S31	-1	1	35	40	5.19
32	S32	1	1	40	60	4.99
33	S33	0	1	45	40	4.75
34	S34	0	1	45	40	4.72
35	S35	0	1	45	40	4.7
36	S36	-1	1	45	80	5.18
37	S37	-1	1	45	0	3.2
38	S38	1	1	50	60	4.23
39	S39	1	1	50	60	4.23

Appendix B4
(Uniaxial tensile test - RSM statistical result data)

Response Surface Regression: Tensile strength versus temperature and
ratio KMnO₄ to AP

Coded Coefficients					
Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	0.82966	0.00913	90.92	0	
Temperature (C)	0.30861	0.00634	-48.64	0	1
Ratio KMnO ₄ to AP	0.11028	0.00634	17.38	0	1
Temperature (C)*Temperature (C)	0.00394	0.00459	0.86	0.397	1.09
Ratio KMnO ₄ to AP*Ratio KMnO ₄ to AP	0.00856	0.00459	-1.87	0.071	1.09
Temperature (C)*Ratio KMnO ₄ to AP	-0.0042	0.011	-0.38	0.707	1

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.0380652	98.78%	98.60%	98.21%

Analysis of Variance					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	3.87475	0.77495	534.83	0
Linear	2	3.86647	1.93324	1334.22	0
Temperature (C)	1	3.42867	3.42867	2366.3	0
Ratio KMnO ₄ to AP	1	0.4378	0.4378	302.15	0
Square	2	0.00807	0.00404	2.79	0.076
Temperature (C)*Temperature (C)	1	0.00107	0.00107	0.74	0.397

Ratio KMnO ₄ to AP*Ratio KMnO ₄ to AP	1	0.00504	0.00504	3.48	0.071
2-Way Interaction	1	0.00021	0.00021	0.14	0.707
Temperature (C)*Ratio KMnO ₄ to AP	1	0.00021	0.00021	0.14	0.707
Error	33	0.04782	0.00145		
Lack-of-Fit	3	0.02458	0.00819	10.57	0
Pure Error	30	0.02324	0.00077		
Total	38	3.92257			

Fits and Diagnostics for Unusual Observations					
Obs	Tensile				
strength					
MPa	Fit	Resid	Std Resid		
6	0.75	0.8297	-0.0797	-2.16	R
9	0.9	1.0192	-0.1192	-3.43	R
16	1.55	1.4626	0.0874	2.67	R
<i>R Large residual</i>					

Appendix B5
(Burn rate test - RSM result data)

RunOrder	Sample	Coded factor		Uncoded factor		Responses
		Pressure (atm) (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Pressure (atm) (V ₁)	Ratio KMnO ₄ to AP (V ₂)	Burn rate (mm/s)
1	S1	1	1	2.5	60	5.71
2	S2	0	1	2	40	6.42
3	S3	1	1	1.5	60	4.62
4	S4	0	1	2	40	6.43
5	S5	-1	1	2	0	4.5
6	S6	-1	1	2	0	4.53
7	S7	0	1	2	40	6.41
8	S8	1	1	2.5	60	4.72
9	S9	-1	1	3	40	7.53
10	S10	-1	1	1	40	4.79
11	S11	-1	1	3	40	7.53
12	S12	0	1	2	40	6.41
13	S13	0	1	2	40	6.42
14	S14	1	1	1.5	20	4.75
15	S15	1	1	2.5	20	6
16	S16	1	1	1.5	60	4.63
17	S17	1	1	2.5	20	6.1
18	S18	0	1	2	40	6.43
19	S19	1	1	2.5	60	5.7
20	S20	0	1	2	40	6.42
21	S21	-1	1	2	0	4.51
22	S22	0	1	2	40	6.43
23	S23	0	1	2	40	6.41
24	S24	0	1	2	40	6.42
25	S25	0	1	2	40	6.43
26	S26	0	1	2	40	6.41
27	S27	-1	1	1	40	4.78
28	S28	1	1	1.5	20	4.76

29	S29	0	1	2	40	6.42
30	S30	-1	1	1	40	4.79
31	S31	-1	1	2	80	4.23
32	S32	-1	1	2	80	4.21
33	S33	1	1	1.5	60	4.61
34	S34	1	1	1.5	20	4.73
35	S35	0	1	2	40	6.43
36	S36	1	1	2.5	20	5.99
37	S37	-1	1	2	80	4.24
38	S38	0	1	2	40	6.43
39	S39	-1	1	3	40	4.72

Appendix B6
(Burn rate test - RSM statistical result data)

Response Surface Regression: Burn rate versus Pressure and ratio KMnO₄ to AP

Term	Coef	SE Coef	T-Value	P-Value	VIF
Constant	6.274	0.121	51.83	0	
Pressure (atm)	0.4711	0.0842	5.6	0	1
Ratio KMnO ₄ to AP	-0.1128	0.0842	-1.34	0.189	1
Pressure (atm) * Pressure (atm)	-0.192	0.0609	-3.15	0.003	1.09
Ratio KMnO ₄ to AP * Ratio KMnO ₄ to AP	-0.522	0.0609	-8.57	0	1.09
Pressure (atm) * Ratio KMnO ₄ to AP	-0.132	0.146	-0.9	0.373	1

Model Summary			
S	R-sq	R-sq(adj)	R-sq(pred)
0.504978	94.00%	92.34%	90.21%

Analysis of Variance					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	5	27.5309	5.5062	21.59	0
Linear	2	8.4479	4.224	16.56	0
Pressure (atm)	1	7.99	7.99	31.33	0
Ratio KMnO ₄ to AP	1	0.4579	0.4579	1.8	0.189
Square	2	18.8749	9.4375	37.01	0
Pressure (atm)*Pressure (atm)	1	2.5344	2.5344	9.94	0.003
Ratio KMnO ₄ to AP*Ratio KMnO ₄ to AP	1	18.7316	18.7316	73.46	0

2-Way Interaction	1	0.208	0.208	0.82	0.373
Pressure (atm)*Ratio KMnO ₄ to AP	1	0.208	0.208	0.82	0.373
Error	33	8.4151	0.255		
Lack-of-Fit	3	2.4941	0.8314	4.21	0.013
Pure Error	30	5.921	0.1974		
Total	38	35.946			

Fits and Diagnostics for Unusual Observations					
Obs	Burn rate (mm/s)	Fit	Resid	Std Resid	
8	4.72	5.787	-1.067	-2.31	R
9	7.53	6.449	1.081	2.5	R
11	7.53	6.449	1.081	2.5	R
39	4.72	6.449	-1.729	-3.99	R
<i>R Large residual</i>					

Appendix B7
(Burn rate test - Burn rate value calculation)

Using equation (28), the burn rate calculation for all the CSP samples are as followed:

$$r = L_p / t_p$$

Where:

r = Burn rate of propellant, (mm/s)

L_p = Propellant length, (mm) = 90 mm

t_p = Propellant burning time, (s)

Sample Pressure	AP CSP				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burning time, t_p (s)	23.19	21.47	20	17.92	16.94
Burn rate equation	$r = 90/23.19$	$r = 90/21.47$	$r = 90/20$	$r = 90/17.92$	$r = 90/16.94$
Burn rate value, r (mm/s)	3.88	4.19	4.5	5.02	5.31
Sample Pressure	KMnO ₄ /AP (20:80) CSP				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burning time, t_p (s)	20.88	18.94	15.81	15	14.26
Burn rate equation	$r = 90/20.88$	$r = 90/18.94$	$r = 90/15.81$	$r = 90/15$	$r = 90/14.26$
Burn rate value, r (mm/s)	4.31	4.75	5.69	6.00	6.31
Sample Pressure	KMnO ₄ /AP (40:60) CSP				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burning time, t_p (s)	18.79	16.33	14.01	12.29	11.9

Burn rate equation	$r = 90/18.79$	$r = 90/16.33$	$r = 90/14.01$	$r = 90/12.29$	$r = 90/11.9$
Burn rate value, r (mm/s)	4.79	5.51	6.42	7.32	7.53
Sample Pressure					
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burning time, t_p (s)	20.97	19.48	16.61	15.76	14.95
Burn rate equation	$r = 90/20.97$	$r = 90/19.48$	$r = 90/16.61$	$r = 90/15.76$	$r = 90/14.95$
Burn rate value r, (mm/s)	4.29	4.62	5.42	5.71	6.02
Sample Pressure					
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burning time (s)	23.8	22.55	21.27	18.71	18
Burn rate equation	$r = 90/23.8$	$r = 90/22.55$	$r = 90/21.27$	$r = 90/18.71$	$r = 90/18$
Burn rate value r (mm/s)	3.78	3.99	4.23	4.81	5.00

Appendix B8
(Mass flow rate calculation)

$$\dot{m} = \rho \cdot A \cdot r$$

Where:

$\dot{m}$ = Mass flow rate of the propellant

ρ = Density of the propellant sample

r = Burn rate of the propellant

A = Area of the burning surface

Taking the area of the burn surface of all the samples as 36 mm² and the volume for calculating the density also is constant as the specifications of the propellant samples are the same which taken as 3240 mm³. The calculation for the mass flow rate of all the CSP samples at various pressures were as followed:

Sample Pressure	AP CSP				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burn rate value, r (mm/s)	3.88	4.19	4.5	5.02	5.31
Mass of the propellant sample, m (g)	15.21	15.21	15.21	15.21	15.21
Propellant density, ρ (g/mm ³)	$\rho = m/V$ $\rho = 15.21/3240$ $\rho = 0.0046$	$\rho = m/V$ $\rho = 15.21/3240$ $\rho = 0.0046$	$\rho = m/V$ $\rho = 15.21/3240$ $\rho = 0.0046$	$\rho = m/V$ $\rho = 15.21/3240$ $\rho = 0.0046$	$\rho = m/V$ $\rho = 15.21/3240$ $\rho = 0.0046$
Mass flow rate, $\dot{m}$ (g/s)	0.64	0.69	0.75	0.83	0.88
Sample Pressure	KMnO ₄ /AP (20:80) CSP				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burn rate value, r (mm/s)	4.31	4.75	5.69	6.00	6.31
Mass of the propellant sample, m (g)	15.34	15.34	15.34	15.34	15.34
Propellant density, ρ (g/mm ³)	$\rho = m/V$ $\rho = 15.34/3240$ $\rho = 0.0047$	$\rho = m/V$ $\rho = 15.34/3240$ $\rho = 0.0047$	$\rho = m/V$ $\rho = 15.34/3240$ $\rho = 0.0047$	$\rho = m/V$ $\rho = 15.34/3240$ $\rho = 0.0047$	$\rho = m/V$ $\rho = 15.34/3240$ $\rho = 0.0047$
Mass flow rate, $\dot{m}$ (g/s)	0.73	0.80	0.96	1.01	1.07
Sample Pressure	KMnO ₄ /AP (40:60) CSP				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burn rate value, r (mm/s)	4.79	5.51	6.42	7.32	7.53
Mass of the propellant sample, m (g)	15.89	15.89	5.89	5.89	5.89
Propellant density, ρ (g/mm ³)	$\rho = m/V$ $\rho = 15.89/3240$ $\rho = 0.0049$	$\rho = m/V$ $\rho = 15.89/3240$ $\rho = 0.0049$	$\rho = m/V$ $\rho = 15.89/3240$ $\rho = 0.0049$	$\rho = m/V$ $\rho = 15.89/3240$ $\rho = 0.0049$	$\rho = m/V$ $\rho = 15.89/3240$ $\rho = 0.0049$

Mass flow rate, $\dot{m}$ (g/s)	0.84	0.97	1.13	1.29	1.32
Sample Pressure	KMnO₄/AP (60:40) CSP				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burn rate value, r (mm/s)	4.29	4.62	5.42	5.71	6.02
Mass of the propellant sample, m (g)	16.02	16.02	16.02	16.02	16.02
Propellant density, ρ (g/mm ³)	$\rho = m/V$ $\rho = 16.02/3240$ $\rho = 0.0049$	$\rho = m/V$ $\rho = 16.02/3240$ $\rho = 0.0049$	$\rho = m/V$ $\rho = 16.02/3240$ $\rho = 0.0049$	$\rho = m/V$ $\rho = 16.02/3240$ $\rho = 0.0049$	$\rho = m/V$ $\rho = 16.02/3240$ $\rho = 0.0049$
Mass flow rate, $\dot{m}$ (g/s)	0.76	0.81	0.96	1.00	1.06
Sample Pressure	KMnO₄/AP (80:20) CSP				
	1 atm	1.5 atm	2 atm	2.5 atm	3 atm
Burn rate value, r (mm/s)	3.78	3.99	4.23	4.81	5.00
Mass of the propellant sample, m (g)	16.29	16.29	16.29	16.29	16.29
Propellant density, ρ (g/mm ³)	$\rho = m/V$ $\rho = 16.29/3240$ $\rho = 0.0050$	$\rho = m/V$ $\rho = 16.29/3240$ $\rho = 0.0050$	$\rho = m/V$ $\rho = 16.29/3240$ $\rho = 0.0050$	$\rho = m/V$ $\rho = 16.29/3240$ $\rho = 0.0050$	$\rho = m/V$ $\rho = 16.29/3240$ $\rho = 0.0050$
Mass flow rate, $\dot{m}$ (g/s)	0.68	0.72	0.76	0.87	0.90

BIODATA OF STUDENT

Mr. Izzat Najmi Bin Mohd Yaacob was born in January 1998 in Kajang, Malaysia. He obtained his Degree in Bachelor of Aerospace Engineering with honors from the Universiti Putra Malaysia, Malaysia in 2021. He subsequently converted his Master's degree in Master of Science to a Doctor of Philosophy (Ph.D.) degree at Universiti Putra Malaysia in 2022. In the same year, he was awarded Tenaga Akademi Muda (TAM) Scholarship Program from Universiti Putra Malaysia to complete his Ph.D. study in the Department of Aerospace Engineering, Faculty of Engineering, UPM.

During his Ph.D. study (2022 – 2024), he has participated in multiple competitions; namely, 3MT Thesis Competition (1st place gold medal award), Gold medal in Malaysia Rocket Competition (university category), and Silver Award for Engineering Innovation & Exhibition 2023 (EIE 2023) in Faculty of Engineering, UPM. He was granted 2 intellectual property (1 copyright and 1 trade secret), has published 3 journal papers and 3 chapter in book on sustainable aerospace field during his doctoral study period. Besides, He is a Graduate Engineer for Board of Engineers Malaysia (BEM) with credential ID G1205196A and a Graduate Technologies for Malaysia Board of Technologies with credential ID GT22020056

LIST OF PUBLICATIONS

Yaacob, I. N. M., Singh, B., Mazlan, N., Gires, E., Basri, A. A., Ismail, O., ... & Ahmad, K. A. (2022). Numerical Study of the AP/Al/HTPB Composite Solid Propellant based Combustion Process in a Small Retro Rocket Motor. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences*, 96(2), 98-114.

Yaacob, I. N., Asli, A. F., Norkhairunnisa, M., Ahmad, K. A., Ismail, O., Salleh, N. A., & Shahedi, S. (2023). A review on viscoelastic behaviour of plasticizers in ap/al/htpb based composite solid propellant. *Materials Today: Proceedings*.

Yaacob, I. N., Mazlan, N., Ahmad, K. A., Basri, A. A., Gires, E., Ismail, O., ... & Shahedi, S. (2023). REDUCTION OF HCl EXHAUST PRODUCTS IN AP/HTPB PROPELLANTS BY DIFFERENT METAL ADDITIVES USING ROCKET PROPULSION ANALYSIS. *EDITORIAL BOARD*, 220, 125.

Shauqi, I., **Yaacob, I. N.**, Hua, T. C., Amir, S. M. M., Rahim, S., Umar, M. Z., ... & Mazlan, N. (2024). Nanoclay Effect on the Ablative Behaviour of Glass Fiber Reinforced Polymer and Glass Fiber Reinforced Geopolymer Nanocomposite Using Radiography. *Journal of Aeronautics, Astronautics and Aviation*, 56(1), 77-83.

Norkhairunnisa, M., Chai Hua, T., Bajuri, F., **Yaacob, I. N.**, & Ahmad, K. A. (2024). Sustainable Biocomposite-Based Biomass for Aerospace Applications. *Plant Biomass Derived Materials: Sources, Extractions, and Applications*, 517-535.

Mazlan, N., Shah, A. U. M., Hua, T. C., **Najmi, I.**, & Ramli, N. (2024). Biocomposites as Aircraft Materials. *Sustainable Materials and Manufacturing Techniques in Aviation*, 27-53.

List of copyright

Lantakas 2.75 inches guidance rocket.

Composite Solid Propellant Composition and Formulation Manual
"KMnO₄/AP dual oxidizer formulation".