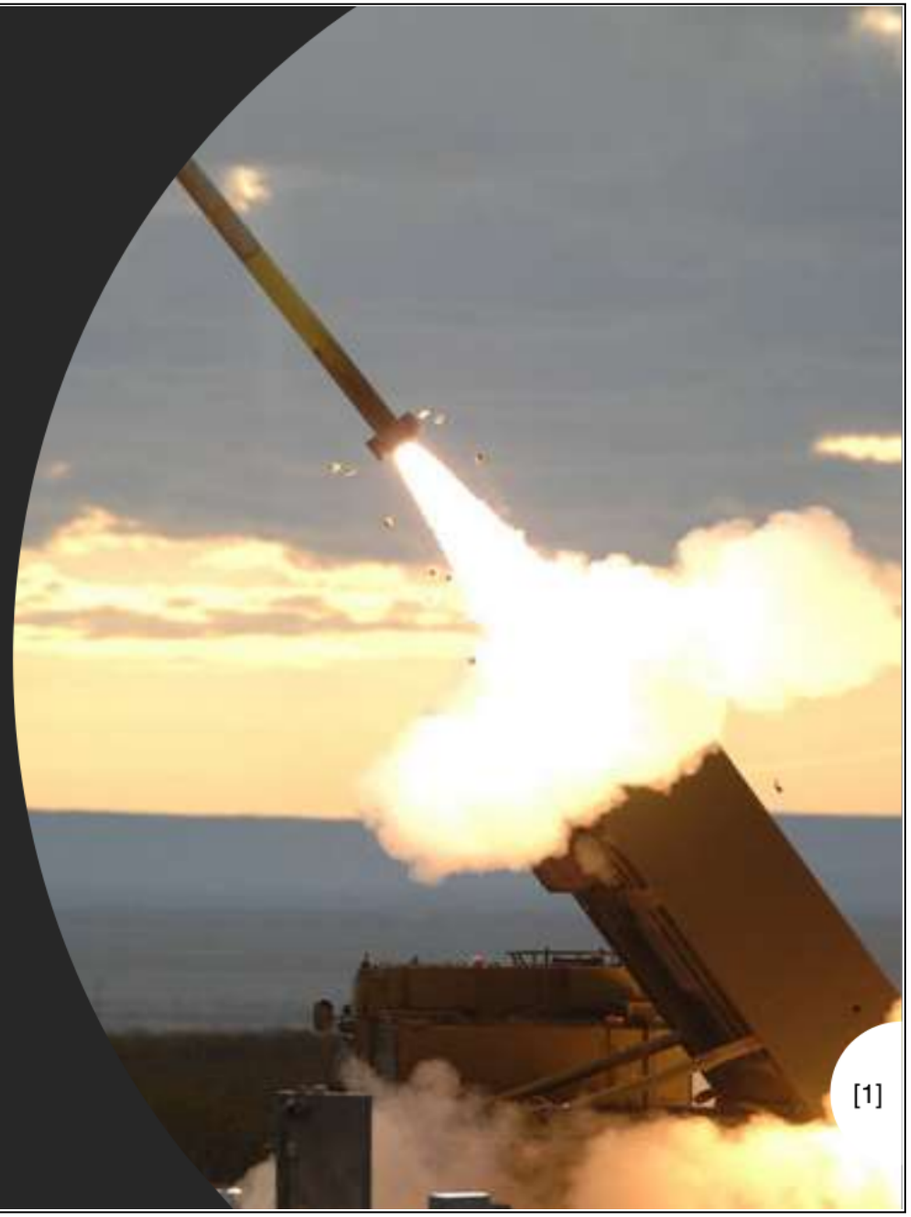
Analysis of Green Propellants

by Ryan Garry

Submission date: 01-Dec-2023 07:57PM (UTC+0000)
Submission ID: 217574164
File name: 27605_Ryan_Garry_Analysis_of_Green_Propellants_544928_911832367.pptx (26.04M)
Word count: 3198
Character count: 20464

Comprehensive Analysis of Green Propellants

Pete Down, Jake Smith, Ryan Garry



[1]

Contents

- Propellant Basics
- Composite Basics
- Green Propellant
- Greener Manufacturing
- Greener Oxidisers
- Conclusion
- References



[2]



[4]

What is a Propellant?

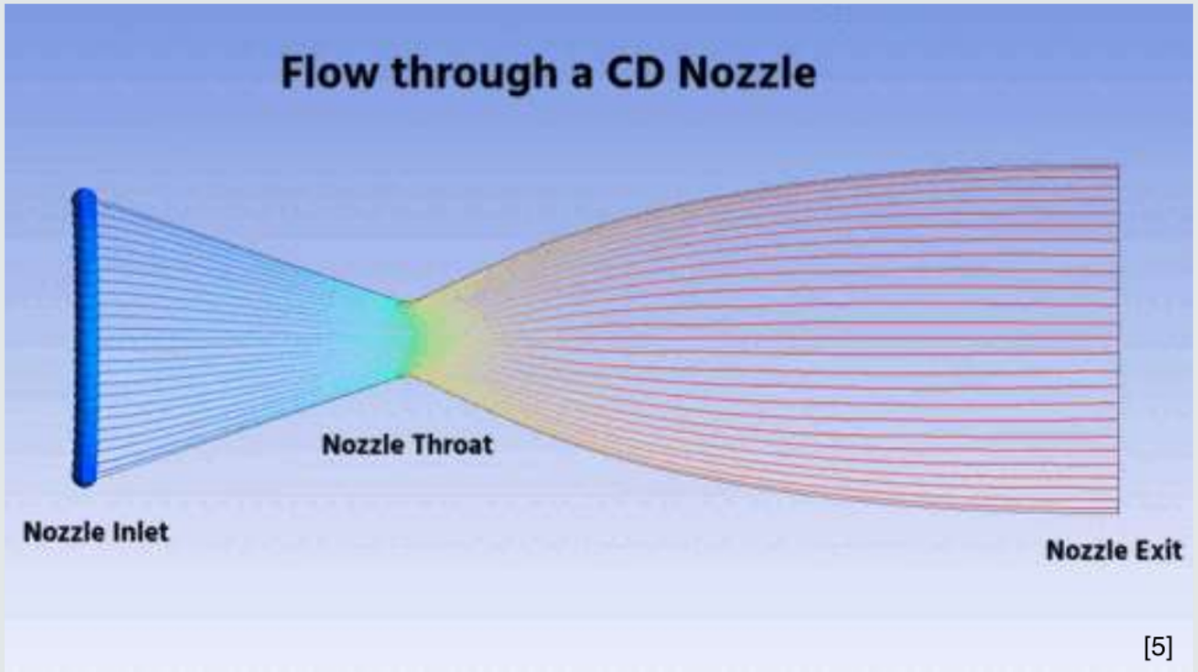
Propellant:

"Any gas, liquid, or solid the expansion of which can be used to impart motion to another substance or object" [3]

How Propellants Work

Gas can be accelerated by:

- Pushing it through a convergent-divergent nozzle
- Heating



[5]

Propellant Basics

- The purpose of a propellant is to accelerate a vehicle or do work within a system using expanding gases.
- Solid or liquid propellants are converted into expanding gas through combustion.
- For Ordnance, Munitions, and Explosive (OME) applications, the primary application of propellants is in rocket motors, artillery, and small arms.

Propellant Variety

Categorised by:

- Chemistry
- Storage configuration
- Application
- System in which it is used
- Key features
- Manufacturing process
- Etc.



Solid Propellant Types

Nitro-glycerine (NG) / Nitrocellulose (NC) based, Composites

- Extruded Double Base (EDB)
- Cast Double Base (CDB)
- Composite Modified Double Base (CMDB)
- Elastomer Modified Cast Double Base (EMCDB)
- Polybutadiene: Hydroxyl-terminated Polybutadiene (HTPB), Aluminium (Al), Ammonium Perchlorate (AP)
- Polybutadiene: HTPB, Ammonium Nitrate (AN), Cyclotetramethylenetetranitramine (HMX), Cyclotrimethylenetrinitramine (RDX), AP
- Polybutadiene: Carboxyl-Terminated Polybutadiene (CTPB), Al, AP
- Polybutadiene: Polybutadiene Acrylonitrile acrylic acid (PBAN), Al, AP
- AN/Polymer

[7, p. 498-499]



Propellant Compositions

- Fuel
- Oxidiser
- Binders
- Plasticisers
- Curing agents
- Stabilisers
- Anti-oxidants
- Additives



Area of Focus

Composite Propellant

What is Composite Propellant?

"Composite propellants form a heterogeneous propellant grain between oxidiser crystals and powdered fuel […] held together in a matrix of synthetic […] binder" [7, p. 492]



[9]

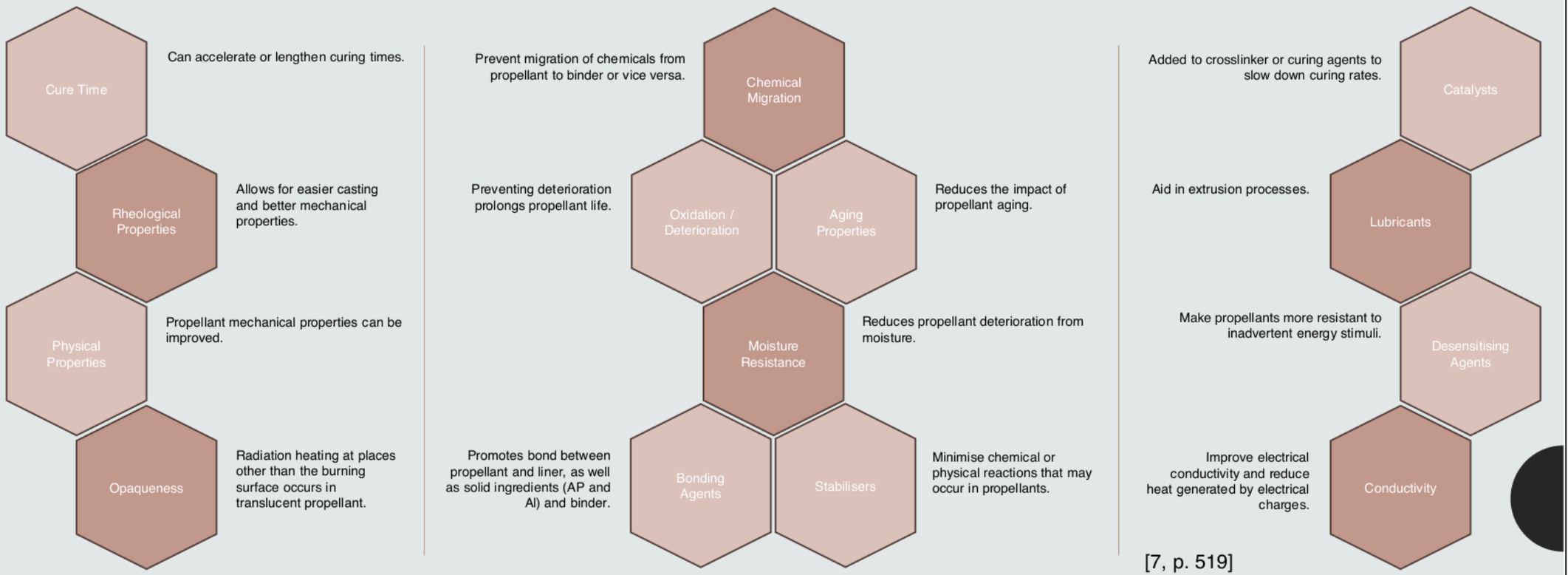
Composite Ingredients

Ingredients for the most common composite propellant:

COMPONENT	PERCENTAGE	INGREDIENT
Oxidiser	0 - 70	• Ammonium Perchlorate (NH_4ClO_4)
Metal Fuel	0 - 30	• Aluminium (Al)
Fuel/binder	5 – 18	• Hydroxyl-terminated Polybutadiene (HTPB)
Curing Agent or Crosslinker	0.2 – 3.5	• Toluene-2,4-diisocyanide (TDI)
Burn Rate Modifier	0.2 – 3	• Ferric Oxide (FeO)
Plasticiser	0 – 7	• Dioctyl Phthalate (DOP)
Bonding Agent	> 0.1	• MAPO-Tartaric Acid-Adipic Acid Condensate (MT-4)
Stabiliser	> 0.5	• Diphenylamine (DPA)

[7, p. 512-513]

Propellant Additives



[7, p. 519]

Composite Propellant

Advantages

- High energy density
- Good Insensitive Munitions (IM) characteristics
- Good performance on EMTAP testing – Safer than alternatives
- Good mechanical properties

[10, Chap. 13, p. 3]

- Stable combustion*
- Non-detonative (class 1.3)*
- Good burn rate control*

[7, p. 498]

Disadvantages

- Low stealth due to large smoke plume
- Toxic products

[10, Chap. 13, p. 3]

- Moisture sensitive*
- High flame temperature*

[7, p. 498]

* Applies specifically to composite with AP, Al, and HTPB (most common type)

Green Propellants



The Twelve Principles of Green Chemistry

The basic definitions of green chemistry was laid down in the 1998 book, Green Chemistry: Theory and Practice [13]. The most relevant definitions are reproduced below:

No.	Title	Description
1	Prevention	It is better to prevent waste than to treat or clean up waste after it has been created.
3	Less Hazardous Chemical Syntheses	Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4	Designing Safer Chemicals	Chemical products should be designed to affect their desired function while minimizing their toxicity.
6	Design for Energy Efficiency	Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
10	Design for Degradation	Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

[13]



[15]

What is a Green Energetic Material?

"A green energetic material is a material designed and manufactured in accordance with the principles of green chemistry, with the minimum requirement to preserve the performance level, and safety of handling, of the energetic material it is intended to replace."

[14]

Why go Green?



Costs



Societal pressure due to public awareness



Legislation - REACH



Safety



Environmental impact


Greener Manufacturing

Manufacturing

"*The principles of green chemistry are largely geared towards guiding the design of the manufacturing process, since for many chemicals the manufacturing has the largest impact on human health and the environment.*" [14]

There are always opportunities to make manufacturing processes greener by:

- Reducing use of energy intensive processes
- Generating green energy
- Reducing waste



[17]

Current Manufacturing Process

Stages of manufacture

- Preparation of the moulds or of the cases
- Mixing operations
- Moulding
- Curing
- Finishing
- Inspection

[19, p. 439]

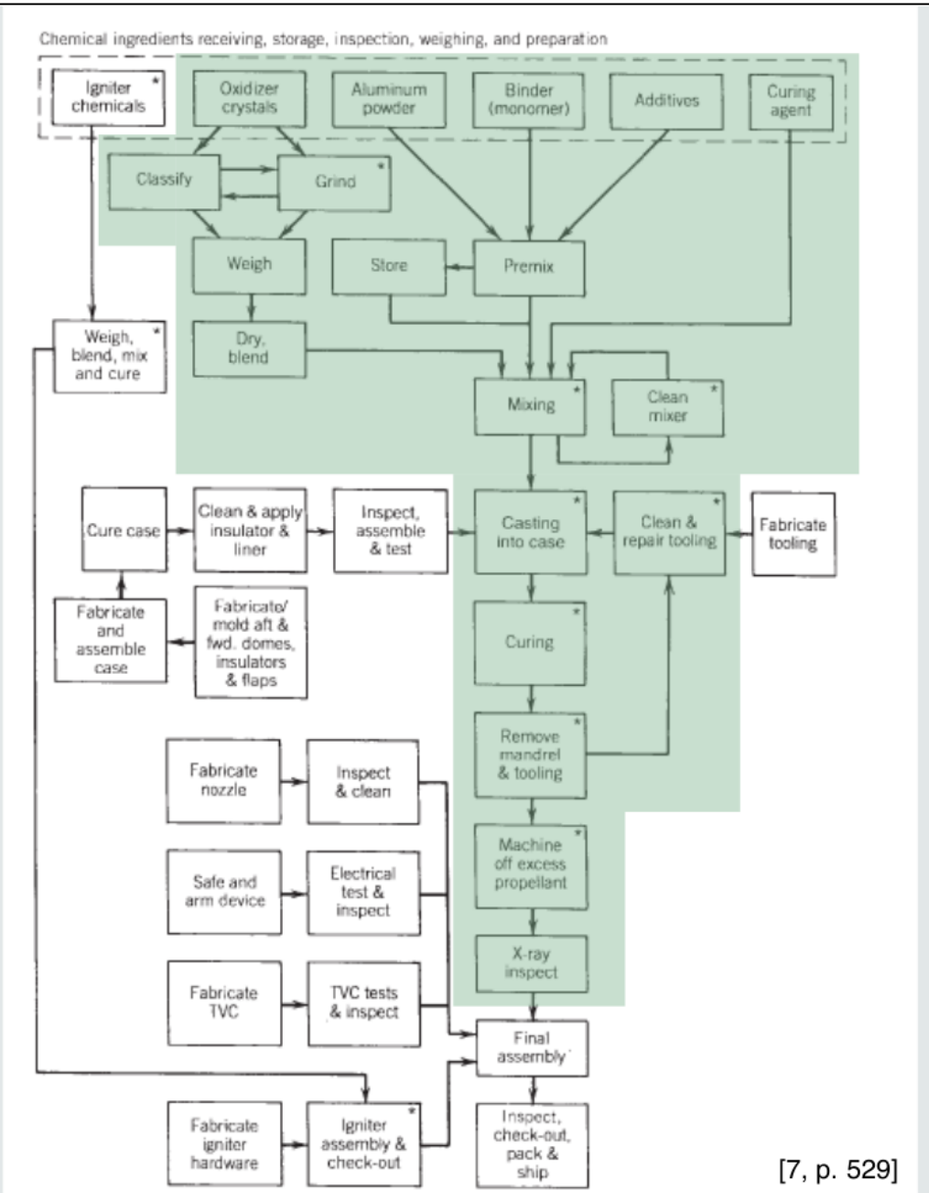


[20]

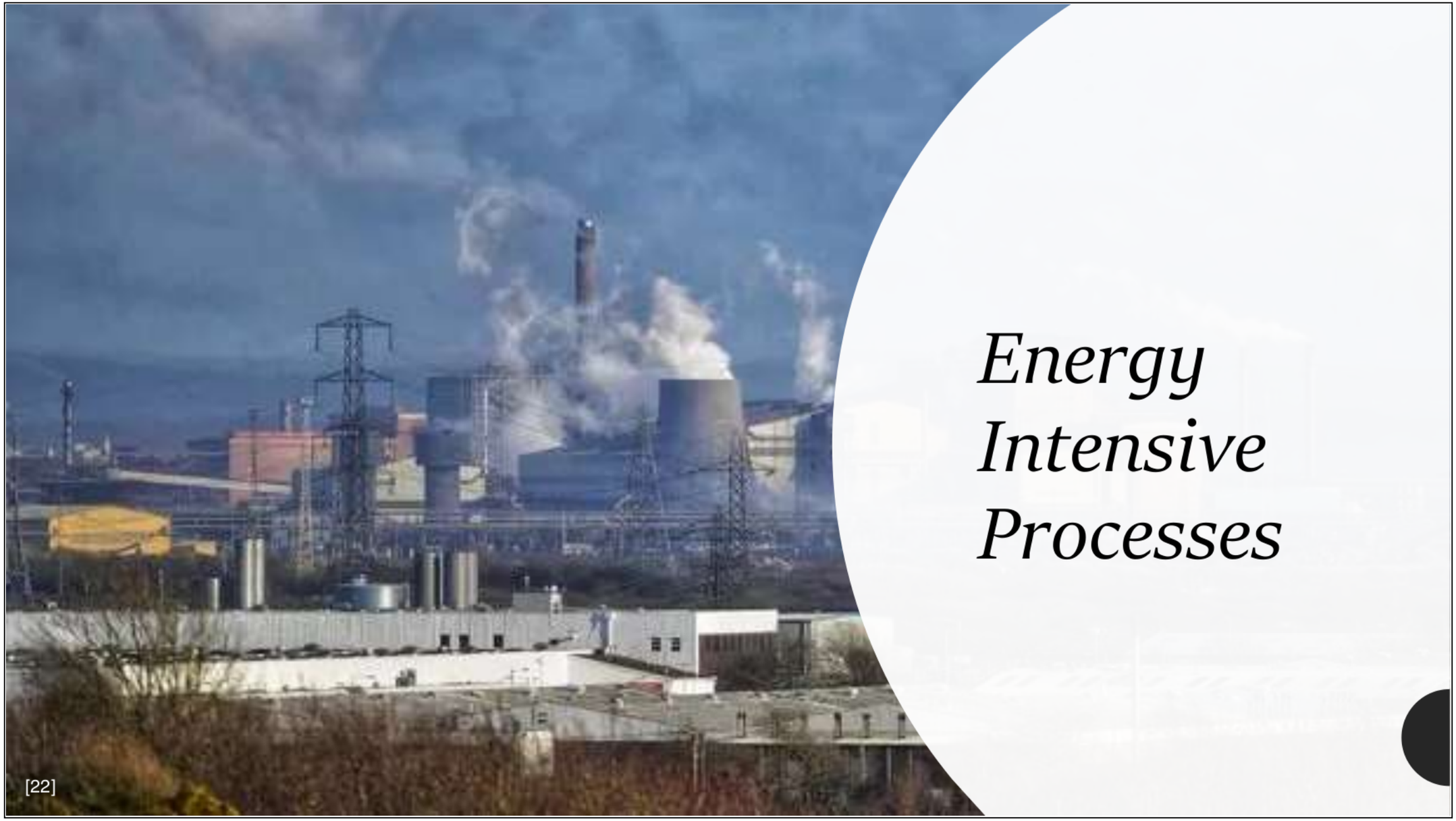


[21]

Current Manufacturing Process



[7, p. 529]



Energy Intensive Processes

[22]



[24]

Energy Intensive Processes

- There are many stages to manufacturing a composite propellant. Many of these stages are energy intensive.
- For example, production of perchlorate crystals (used in ammonium perchlorate (AP) production) via electrolysis uses between 26 and 56 kWh per kilogramme depending on concentration [23].

To Put that into Perspective...

Each solid rocket booster (SRB) contains 500,000 kg of propellant [25]. The propellant is 70% AP [26]. Therefore, the energy needed to produce enough perchlorate for this can be calculated as:

For two SRBs the total weight of AP is 698,532 kg.

To produce that much AP, you would require between 18 and 39 TWh of energy.

This is enough energy to power an average home in the U.S. for between 1657 and 3572 years! [27]



[28]


Green Energy Generation



[30]

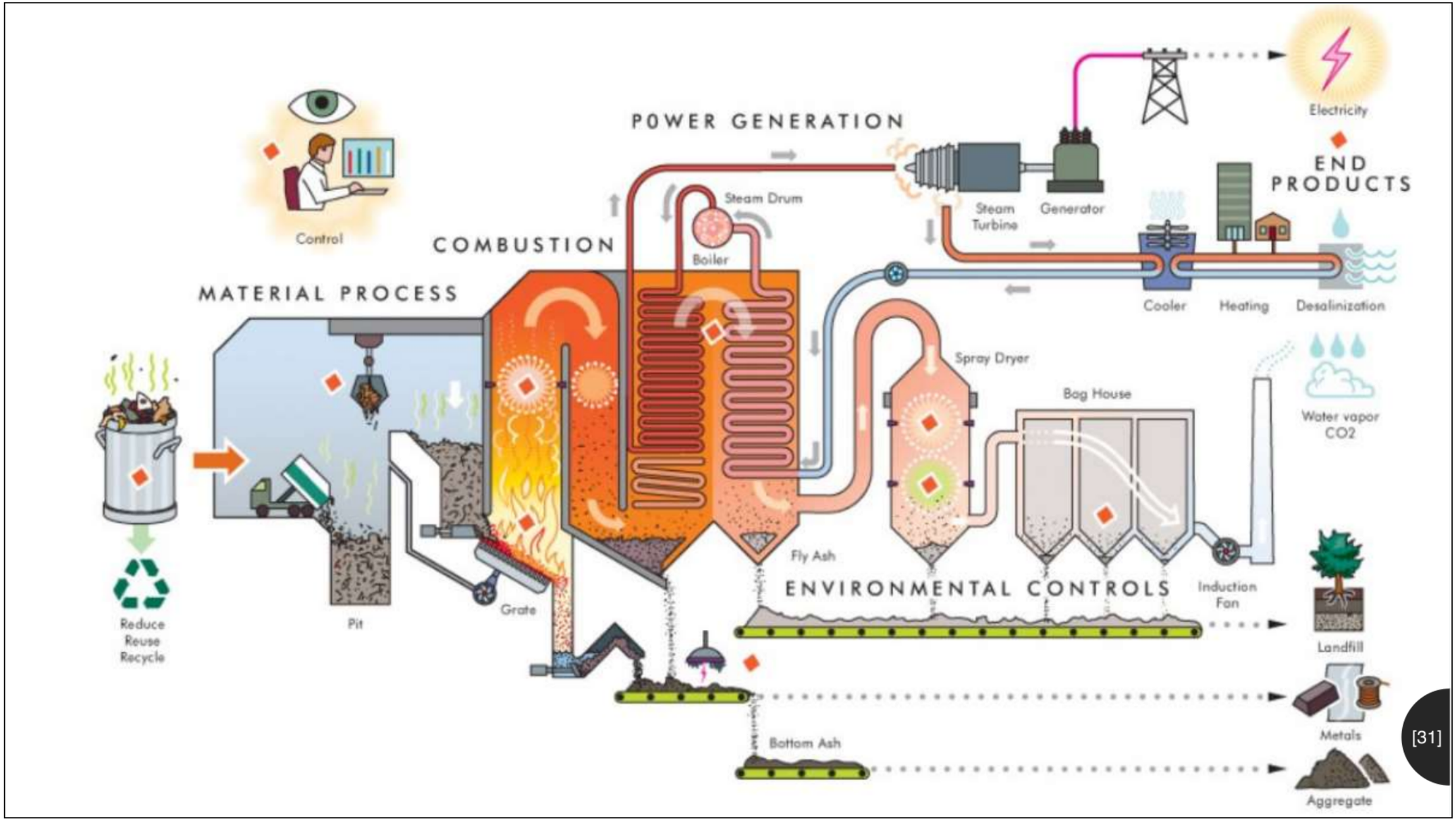
Process Wastage

- All propellant manufacturing processes produce waste material.
- Such material is not reusable nor recyclable.
- It must be destroyed as soon as possible as it poses a safety hazard.
- This is currently done through open burning.



Solution: Energetic Incinerator

[30]


Control
POWER GENERATION
Electricity
END PRODUCTS
Steam Drum
Steam Turbine
Generator
COMBUSTION
Boiler
MATERIAL PROCESS
Cooler
Heating
Desalinization
Spray Dryer
Bag House
Water vapor CO2
Fly Ash
ENVIRONMENTAL CONTROLS
Induction Fan
Reduce Reuse Recycle
Pit
Grate
Landfill
Metals
Bottom Ash
Aggregate



Toxicity

- Many of the highest performing propellant ingredients are toxic.
- Using such materials creates a hazard to health and may lead to environmental contamination.

Toxicity is an issue which propellant manufacturers must deal with because:

- Repeated Range firings of toxic propellants will lead to a build-up of toxic products.
- There is a greater risk of soil and water contamination around the manufacturing site.

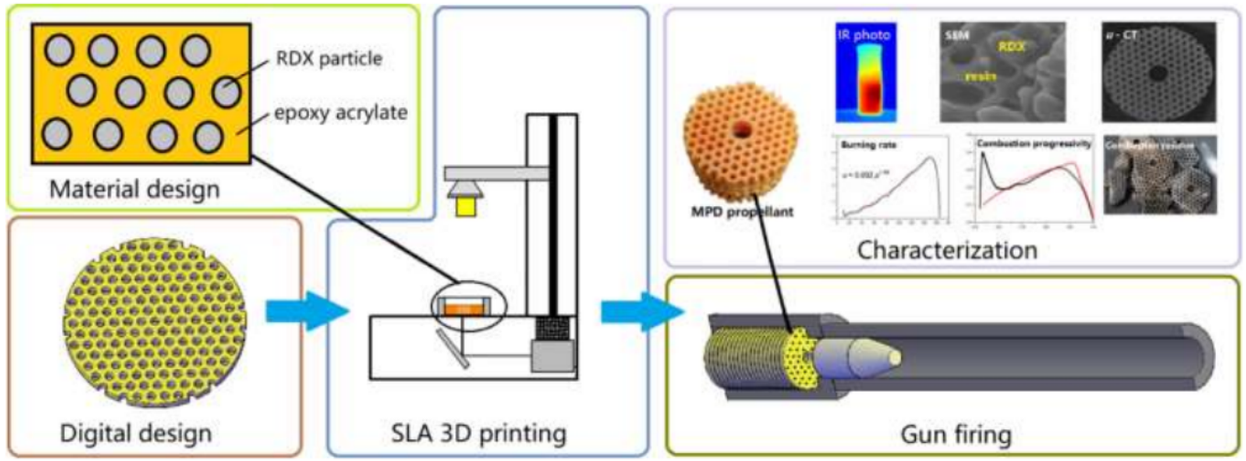
Example: Perchlorates

- For many years, the U.S. Environmental Protection Agency (EPA) has been trying to regulate perchlorate contamination in water.
- The primary source of perchlorates in the environment is propellants and other types of explosive [32].
- At least 35 U.S. states are estimated to have drinking water contaminated by perchlorates [33].
- The EPA advise a maximum limit of 15 ppb of perchlorate for drinking water [14].

Perchlorate exposure may have the following health effects [34]:

- Reduced thyroid iodide uptake
- Increased serum iodide levels
- Increased urinary iodide excretion

- One way to prevent perchlorate groundwater contamination is to stop using perchlorate oxidisers in propellant.



[35]

Future Manufacturing Methods

- 3D printing of propellants is a novel method of propellant manufacture.

The advantages of 3D printing propellants are [35]:

- Minimise wastage
- Make propellant grains with specific non-traditional shapes
- Small batch production at low prices
- Reduces time from fabrication to propellant operation which allows for improvement in R&D processes.
- Miniaturisation, weight reduction, and integration of propellant and other components

Greener Oxidisers



[36]

Oxidisers - AP

Ammonium Perchlorate is currently the most used oxidiser in composite rocket propellant. AP is not a green propellant for two reasons:

1. Combustion produces hydrogen chloride - Up to about 14% of the combustion product can be hydrogen chloride which reacts with water in the atmosphere to form hydrochloric acid (HCl) [7, p. 510]. HCl contributes to acid rain and ozone depletion [14, p. 6]
2. Perchlorates can be inadvertently released into the environment – This can occur through incomplete combustion or leakage from undisposed material. Once perchlorates enter the drinking water supply, high intakes may lead to thyroid disorders. In the USA, the Environmental Protection Agency advises a maximum limit of 15 ppb for drinking water [14, p. 6].

Green Oxidisers

Ammonium perchlorate is predominantly used across industry for its beneficial properties.

Many other oxidisers are currently being researched which could replace AP

These oxidisers tend to be greener.

Ammonium Dinitramide (ADN)

ADN is considered a possible replacement for AP because:

- It has a high specific impulse [38].
- It is considered a green energetic material as it possesses a non-chlorinated exhaust [38].
- It has a high burning rate [38].
- It has good ballistic properties below 100 atmospheric pressure (atm) [38].
- It is unable (pure ADN) to combust at atmospheric pressures which improves process safety. Combustion was only experimentally achieved at atmospheric pressure with molten ADN at 100 °C [38].

ADN Manufacture

Synthesized through nitration of various Ammonium salts, Ammonia, or Ethyl Carbamate. It is followed by neutralisation and separation of ADN from byproducts formed [10, Chap. 2, p. 42].

It has been suggested that it could be formed without neutralisation using cyanoguidine in nitration mixture, which also allows for spent acids to be regenerated and minimises harmful byproducts during manufacture [39].

Problems with ADN

- Incompatible with isocyanates which are the best cross-linking agents for HTPB. This can be overcome with a mixture of stabilisers. ADN/HTPB propellants have been formulated, however the performance and mechanicals are poor. Therefore, newer energetic binders tend to be used such as Glycidyl Azide Polymer (GAP) [38].
- Lower density than AP [38].
- Lower oxygen balance than AP (26% vs 34%) [38].
- Negative particle size effect as binder acts as a heat sink for smaller particles of ADN [38].
- High hygroscopicity because of shorter hydrogen bonds [39]. ADN is subject to deliquescence [41].
- Low critical relative humidity (RH) at 25 °C is 55.2% [38]. For comparison, the critical RH of AP is 75% [40]. Encapsulation requires the ADN to be completely dry and is thus made more difficult because of the low RH of ADN [42].
- 14% shrinkage on solidification [38]. Makes manufacture into a rocket motor complicated.
- Ammonium nitrate (AN) forms a eutectic mixture with ADN during storage which can drop the melting point below 93 °C [38].

Tetranitroacetemic Acid (TNAA)

TNAA is considered a possible replacement for AP because:

- Environmentally friendly decomposition products [43].
- High oxygen balance (30%) [43].
- Acceptable melting point of 91 °C [43].
- Lower impact sensitivity than AP [43]
- High specific impulse (209 s) [43].
- Easily synthesized by reaction of FOX-7 and fuming nitric acid [43].

Hydrazinium Nitroformate (HNF)

HNF is considered a possible replacement for AP because:

- High enthalpy of formation compared to AP [44].
- High specific impulse (254.37) [44].
- Significantly greater combustion temperature than AP which improves the energy release of the propellant [44].
- No chlorides in combustion products [44] so can be considered a green propellant.

It is synthesised through nitration and neutralisation of intermediate nitroform prepared from Isopropyl Alcohol [45].

Problems with HNF

HNF attacks binder chains of HTPB, forming pockets of gas and softening material. Due to this combined effect the propellant swells. This reduces shelf life to only be days long. As a result, other binders must be used (E.g. GAP, Poly-NIMMO) [46].

Poor thermal stability [10, Chap. 13, p. 31] resulting in faster decomposition [47].

Comparison of Oxidisers

Material	Melting Point (°C)	Oxygen Balance (%)	Density (kg/m^3)	Specific Impulse (s)	Primary Issue
AP [38]	> 200	+35	1950	159	Toxic product
ADN [38]	93	+26	1813		Hygroscopic
TNAA [43]	91	+30	2044	209	High cost
HNF [44]	123	+13	1900	260	Poor thermal stability

Conclusions

- Green energetic materials are being adopted as they have a lower unit cost, make manufacturing safer, and prevent damage to the environment. Additionally, pressure is being put on the propellant industry to adopt green propellants by the public and by governments via regulation.
- There are alternative oxidisers to ammonium perchlorate that provide equivalent or improved performance while being considered green energetic materials. However, these materials come with their own technical issues that will need to be overcome to make them viable and commonplace oxidisers.
- Using green energy significantly reduces the environmental impact of propellant manufacturing. There are ways to use up waste from the manufacturing process and recapturing its energy to offset the environmental impact of energy intensive manufacturing.


Questions

References

[1] K. Kesner, "Lockheed delivers 20,000th Guided MLRS rocket, also called Army's '70-kilometer sniper rifle'," The Huntsville Times, 06 08 2012. [Online]. Available: https://www.al.com/huntsville-times-business/2012/08/lockheed_delivers_20000th_guid.html.

[2] Royal Australian Navy, "RIM-162 Evolved Sea Sparrow Missile," [Online]. Available: https://www.navy.gov.au/weapon/rim-162-evolved-sea-sparrow-missile.

[3] Britannica, "propellant," [Online]. Available: https://www.britannica.com/science/propellant.

[4] Fraunhofer ICT, "Propellants for rockets and guns," [Online]. Available: https://www.ict.fraunhofer.de/en/comp/em/treib.html.

[5] "Flow characteristics of convergent divergent nozzle at supersonic and subsonic speeds," kcgcollege, [Online]. Available: https://kcgcollege.ac.in/Virtual-Lab/Aeronautical/round-template/experiment/simulation/index.html.

[6] A. Parsonson, "HyImpulse Qualifies Hybrid Rocket Motor for Flight," European Spaceflight, 7 09 2023. [Online]. Available: https://europeanspaceflight.com/hyimpulse-qualifies-hybrid-rocket-motor-for-flight/

[7] G. P. Sutton and O. Biblarz, Rocket Propulsion Elements Ninth Edition, Hoboken, New Jersey: John Wiley & Sons, Inc., 2017.

[8] "Space Shuttle Projects," NASA Image and Video Library, 13 07 1979. [Online]. Available: https://images.nasa.gov/details-7997301.

[9] "Rockets and rocket launches information and facts," supergtrmk, [Online]. Available: https://supergtrmk.live/product_details/49014991.html.

[10] JSP 333 Services Textbook of Explosives, DE&S Wpns Tech Info & Docs Pubs Mgr, 2020.

[11] UK Space Facilities, "Typical propellant charges," [Online]. Available: https://www.ukspacefacilities.stfc.ac.uk/Gallery/Propellant%20charges.jpg.

[12] Sky News, "Elon Musk 'highly confident' that SpaceX's Starship will launch into orbit this year," 11 02 2022. [Online]. Available: https://news.sky.com/story/elon-musk-highly-confident-that-spacexs-starship-will-launch-into-orbit-this-year-12538984.

[13] P. Anastas and J. Warner, Green Chemistry: Theory and Practice, Oxford University Press, 1998.

References

[14] T. Brinck, Green Energetic Materials, John Wiley & Sons Ltd, 2014.

[15] I. Palarwal, "Green Future; Sustainable Technology," Medium, 15 08 2023. [Online]. Available: https://medium.com/@palarwalisha/green-future-sustainable-technology-b4def8e3e986.

[16] K. Rutledge, "Air Pollution," National Geographic, 19 10 2023. [Online]. Available: https://education.nationalgeographic.org/resource/air-pollution/.

[17] NASA's Marshall Space Flight Center, "Recipe for Power," 11 02 2015. [Online]. Available: https://www.youtube.com/watch?v=H0BgLPq6PkE.

[18] S. Barry, "Tata says Port Talbot steelworks under threat without UK Government financial support," Business Live, 22 07 2022. [Online]. Available: https://www.business-live.co.uk/manufacturing/tata-says-port-talbot-steelworks-24558851.

[19] A. Devanas, Solid Rocket Propulsion Technology, Oxford: Pergamon Press Ltd., 1993

[20] als_liahona, "3D Printed Funnels for Rocket Motor Propellant Casting," Autodesk Instructables, [Online]. Available: https://www.instructables.com/3D-Printed-Funnels-for-Rocket-Motor-Propellant-Cas/.

[21] "Solid Propellants," Andoya Space, 2023. [Online]. Available: https://learn.andoyaspace.no/ebook/student-rocket-pre-study/rocket-propellants-2/solid-propellants/.

[22] S. Barry, "Tata says Port Talbot steelworks under threat without UK Government financial support," Business Live, 22 07 2022. [Online]. Available: https://www.business-live.co.uk/manufacturing/tata-says-port-talbot-steelworks-24558851.

[23] J. Llanos, I. Morelada, C. Saez, M. A. Rodrigo and P. Canizares, "Electrochemical production of perchlorate as an alternative for the valorization of brines," Chemosphere, vol. 220, p. 637, 2019.

[24] "Potential and Kinetic Energy Explained," Just Energy, [Online]. Available: https://justenergy.com/blog/potential-and-kinetic-energy-explained/.

[25] T. D. Wood, "Solid Rocket Booster (SRB) Flight System Integration at Its Best," NASA, Huntsville.

References

[26] M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe and A. Subhananda Rao, "Environmentally compatible next generation green energetic materials (GEMs)," Journal of Hazardous Material, vol. 161, p. 596, 2009.

[27] "How much electricity does an American home use?," US Energy Information Administration, 20 10 2023. [Online]. Available: https://www.eia.gov/tools/faqs/faq.php?id=97&t=3.

[28] C. Ward, "The Most Memorable Space Shuttle Missions Ever," Slash Gear , 21 08 2023. [Online]. Available: https://www.slashgear.com/765028/the-most-memorable-space-shuttle-missions-ever/.

[29] S. Ingrams, "What is renewable energy?," Which?, 28 11 2023. [Online]. Available: https://www.which.co.uk/reviews/energy-companies/article/green-energy-suppliers/what-is-renewable-energy-a9qL68h8ziok.

[30] E. Lopez, "Explosive waste incinerator at Picatinny reduces need for open burning," US Army, 12 09 2012. [Online]. Available: https://www.army.mil/article/87001/explosive_waste_incinerator_at_picatinny_reduces_need_for_open_burning.

[31] U.S. Energy Information Administration, "Biomass explained," 08 12 2022. [Online]. Available: https://www.eia.gov/energyexplained/biomass/waste-to-energy-in-depth.php.

[32] L. Friedman, "E.P.A. Decides Against Limiting Perchlorate in Drinking Water," The New York Times, 31 03 2022. [Online]. Available: https://www.nytimes.com/2022/03/31/climate/epa-perchlorate-drinking-water.html.

[33] E. Schor, "As EPA Moves to Regulate Perchlorate, Groups Await Pentagon Response," The New York Times, 04 10 2010. [Online]. Available: https://archive.nytimes.com/www.nytimes.com/gwire/2010/10/04/04greenwire-as-epa-moves-to-regulate-perchlorate-groups-aw-43754.html.

[34] Agency for Toxic Substances and Disease Registry, "Toxicological Profile For Perchlorates," U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, 2008

[35] Y. Weitao, R. Hu, L. Zheng, G. Yan and W. Yan, "Fabrication and investigation of 3D-printed gun propellants," Materials and Design, vol. 192, p. 2, 2020.

[36] Army Technology, "Finnish Army tests multiple launch rocket system GMLRS ammunition," 25 11 2020. [Online]. Available: https://www.army-technology.com/news/finnish-army-tests-multiple-launch-rocket-system-gmlrs-ammunition/.

References

[37] CNBC, "India's friction with U.S. rises over planned purchase of Russian S-400 defense systems," 15 01 2021. [Online]. Available: https://www.cnbc.com/2021/01/15/india-us-friction-rises-over-russian-s-400-defense-systems-.html.

[38] P. Kumar, "An overview on properties, thermal decomposition, and combustion behavior of ADN and ADN based solid propellants," Defence Technology, vol. 14, p. 661, 2018.

[39] A. Rahman, "Synthesis and Performance Analysis of Ammonium Dinitramide".

[40] Y. Nishiwaki, T. Matsunaga and M. Kumasaki, "Study of the hygroscopic deterioration of ammonium perchlorate/magnesium mixture," Sci. Tech. Energetic Materials, vol. 79, no. 1, p. 19, 2018.

[41] T. Shichao, Y. Wang, X. Chen, D. Hu, Y. Hu, S. Zheng, Z. Zhou, C. Xiao and Z. Ren, "Anti-hygroscopicity technologies for ammonium dinitramide: A review," Propellants, Explosives, Pyrotechnics, vol. 48, no. 5, 2023.

[42] A. Larsson and N. Wingborg, "Green Propellants Based on Ammonium Dinitramide (ADN)," in Advances in Spacecraft Technologies, Rijeka, InTech, 2011, pp. 139-156.

[43] X. Zhang and X. Gong, "A computational study on new oxidizers as replacements for ammonium perchlorate: tetranitroacetimidic acid and tetranitroacetamide," Canadian journal of chemistry, vol. 95, no. 2, pp. 199-206, 2017.

[44] L.-n. Zhang, Q.-q. Lin, B.-d. Cheng, P.-c. Wang, M. Lu and Q.-h. Lin, "Effect of hexanitroethane (HNE) and hydrazinium nitroformate (HNF) on energy characteristics of composite solid propellants," FirePhysChem, vol. 1, pp. 116-122, 2021.

[45] P. Ding, H. Wang, L. Wen, G. Cheng, C. Lu and H. Yang, "Studies on Synthetic Technology and Reduced Sensitivity Technology of Hydrazinium Nitroformate," Industrial & Engineering Chemistry Research, vol. 53, pp. 13851-13855, 2014.

[46] G. da Silva, S. C. Rufino and K. Iha, "Green Propellants: Oxidizers," Journal of Aerospace Technology and Management, vol. 5, no. 2, pp. 139-144, 2013.

[47] M. A. Bohn, "Thermal Stability of Hydrazinium Nitroformate (HNF) Assessed by Heat Generation Rate and Heat Generation and Mass Loss," Journal of Pyrotechnics, no. 26, pp. 65-94, 2007.

[48] E. Sauers, "Get ready: SpaceX Starship will try to fly again soon," Mashable, 16 11 2023. [Online]. Available: https://mashable.com/article/spacex-starship-launch-date.

[49] E. Berger, "Sorry, doubters: Starship actually had a remarkably successful flight," ARS Technica, 20 11 2023. [Online]. Available: https://arstechnica.com/space/2023/11/heres-why-this-weekends-starship-launch-was-actually-a-huge-success/.

Analysis of Green Propellants

GRADEMARK REPORT

FINAL GRADE

68/100

GENERAL COMMENTS

Engagement with literature (8/10)

You demonstrated excellent engagement with literature by selecting variety of relevant and credible sources.

IEEE format applied to all references.

In your future presentations/reports/etc use recent (within 5 years) sources and choose more books/journal articles than websites.

Knowledge and understanding skills (19/30)

Your general knowledge of possible replacements for AP propellants and potential issues related to them is very good and well supported by data (EPA).

It would be good to use more specific examples (e.g. what companies use these substitutes? what is the rate of success? etc.).

Cognitive and intellectual skills (18/30)

You showed very good judgment of the current situation and the dilemma that have to be addressed to make the propellants more environmentally friendly.

Practical skills (17/20)

You clearly linked the content of your presentation to a real world research activity.

You answered the question with high level of confidence

Transferable skills (6/10)

Very well prepared and delivered presentation.

Very good team work but the workload not shared equally

For the next group project make sure that content and time are evenly distributed between all working together .

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6

PAGE 7

PAGE 8

PAGE 9

PAGE 10

PAGE 11

PAGE 12

PAGE 13

PAGE 14

PAGE 15

PAGE 16

PAGE 17

PAGE 18

PAGE 19

PAGE 20

PAGE 21

PAGE 22

PAGE 23

PAGE 24

PAGE 25

PAGE 26

PAGE 27

PAGE 28

PAGE 29

PAGE 30

PAGE 31

PAGE 32

PAGE 33

PAGE 34

PAGE 35

PAGE 36

PAGE 37

PAGE 38

PAGE 39

PAGE 40

PAGE 41

PAGE 42

PAGE 43

PAGE 44

PAGE 45

PAGE 46

PAGE 47