Sodium Borohydride as Alternative Fuel for Maritime Vessels

van Benten, M.C.; Padding, J.T.; Schott, D.L.

Publication date
2024

Document Version
Accepted author manuscript

Citation (APA)
van Benten, M. C., Padding, J. T., & Schott, D. L. (2024). *Sodium Borohydride as Alternative Fuel for Maritime Vessels*. 583-588. Paper presented at European PhD Hydrogen Conference, Ghent, Belgium.

Sodium Borohydride as Alternative Fuel for Maritime Vessels

M.C. van Benten* [1], J.T. Padding[2], D.L. Schott[1]

[1]Maritime and Transport Technology, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, 2628CD, the Netherlands
[2]Process and Energy, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, 2628CD, the Netherlands

Introduction

Greenhouse gas emissions are responsible for global warming [1], and this could lead to significant and irreversible damage to the natural ecosystem and human society. As the maritime sector accounts for approximately 3% of the global emissions [2], the International Maritime Organization (IMO) posed restrictions on the emissions of the maritime sector to pursue a decrease of emissions of 40% by 2030, and 70% by 2050, with respect to 2008 [3]. This could be achieved by increasing the efficiency of maritime vessels [4], e.g. by designing modular power plants for maritime vessels [5]. Another option is to switch to alternative fuels such as hydrogen [6]. Traditionally, hydrogen is compressed and stored as a gas, liquefied, or cryo-compressed (liquefied under high pressure). However, each of these methods has drawbacks such as high pressures, low volumetric density, high energy requirements, and thick (insulated) walls. To overcome these disadvantages, alternative methods to store hydrogen are increasingly researched. Alternative methods, where hydrogen is stored in a carrier material, can be sorted into two different categories: liquid hydrogen carriers and solid hydrogen carriers. There are multiple viable hydrogen carriers, but the solid hydrogen carrier sodium borohydride ($NaBH_4$), which is a granular material, is particularly promising [7]. It is non-flammable, can be stored at ambient conditions (pressure and temperature), and has a relatively high volumetric energy density [8–10] compared to traditional hydrogen storage. When using $NaBH_4$ as fuel for maritime vessels, it reacts with water inside a reactor to produce hydrogen and a reaction product (spent fuel). The latter has to be stored for the remainder of the voyage and can be regenerated onshore. Both the $NaBH_4$ and its spent fuel are granular materials that can be classified as granulate or powder, depending on the size of their particles. While Lensing [11], Nievelt [12], and Düll et al. [13] investigated the use of $NaBH_4$ and other solid hydrogen carriers for maritime vessels, they did not discuss their mechanical characteristics which are required to design suitable storage and handling equipment.

This paper aims to identify the required mechanical characteristics of $NaBH_4$ and its spent fuel, to be able to design equipment for handling and storage using the Discrete Element Method (DEM). First, a circular bunkering process will be discussed, providing insight into the required storage and handling equipment. Then, a methodology to determine the required mechanical characteristics of $NaBH_4$ and its spent fuel is presented. Finally, a conclusion is given, and how the empirically determined data can be used for modelling equipment with DEM is discussed.

*Corresponding author: M.C.vanBenten@tudelft.nl

Circular Bunkering Process

In Figure 1, the required circular bunkering process to bunker multiple vessels simultaneously is shown. First, the fuel ($NaBH_4$), is stored in the port storage, from where it can be transported to the onboard fuel storage of the vessels when moored along the quay. During vessel operation, $NaBH_4$ is mixed with water and fed to the reactor, where it is converted into hydrogen (H_2), and a reaction product (spent fuel), conform Equation 1 [14]:

$$\mathrm{NaBH_4 + (2+x)H_2O \rightarrow NaBO_2 \cdot xH_2O + 4H_2} \qquad \text{for } x \in [0, 2, 4] \tag{1}$$

While the obtained hydrogen is used to power the vessel, the spent fuel ($NaBO_2{\cdot}xH_2O$) has to be stored. First, the spent fuel, also known as sodium metaborate, is separated by crystallisation from the unreacted fuel and water, where after it can be stored in the vessel's spent fuel storage. When the vessel receives new fuel, the spent fuel has to be transported to the port storage to be able to execute a new mission. At the port, the spent fuel can be regenerated into the fuel, as shown in Equation 2 [15, 16]:

$$\mathrm{NaBO_2 \cdot xH_2O + (2+x)MgH_2 \rightarrow NaBH_4 + (2+x)MgO + (2x)H_2} \quad \text{for } x \in [0, 2, 4] \tag{2}$$

where $\mathrm{MgH_2}$ and MgO denote magnesium hydride, magnesium oxide, and magnesium, respectively. The design, configuration, and capacity of vessels' and port storage facilities and handling equipment for both the fuel and the spent fuel depends on numerous factors, such as the number of vessels N, the type of vessels, and the behaviour of the materials. The latter can be quantified by measuring the mechanical characteristics of the materials, which will be discussed in the next section.

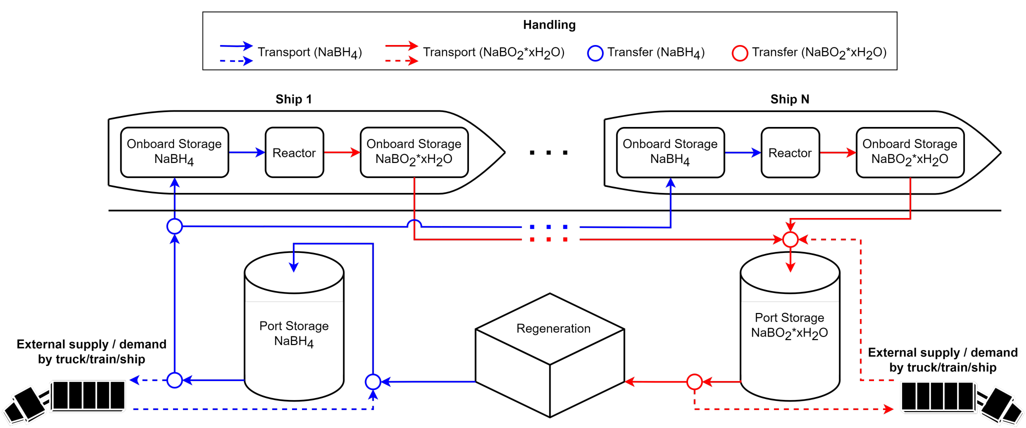

Figure 1: Circular Bunkering Process

Mechanical Characteristics of Bulk Materials

In a previous paper, we defined three categories of mechanical characteristics [17]: bulk material characteristics, interface characteristics, and particle characteristics. The former describes the characteristics of the bulk material and the interaction with itself, such as bulk density, particle size distribution, internal friction and cohesion, while the interface characteristics describe the interaction of the bulk material with the equipment, such as the wall friction or adhesion. The last category, particle characteristics, focuses on the individual particles, e.g. their density, size, and shape. Furthermore, these mechanical characteristics are not fixed but are affected

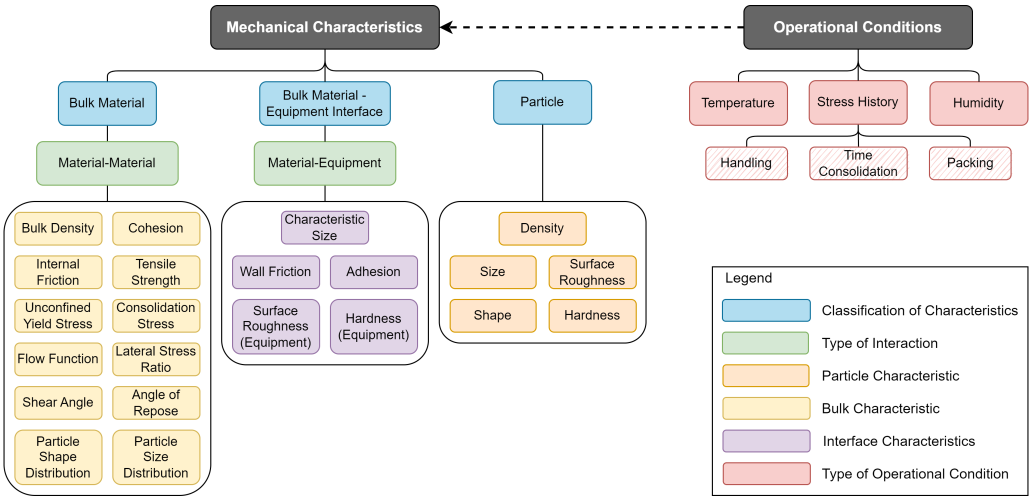

Figure 2: Mechanical Characteristics and Operation Conditions [17]

by operational conditions such as temperature, stress history, and humidity. Temperature and humidity affect the moisture content of bulk materials, which in turn affect their cohesion and adhesion through capillary forces [18]. Next to this, temperature changes can result in the expansion or contraction of individual particles [19], effectively altering the particle size, bulk density, and other characteristics. Stress history, including handling, time consolidation, and packing, affects the mechanical characteristics mainly due to prolonged and varying stresses applied to the particles. Handling could result in changing particle size and shape distributions due to attrition and breakage of particles [20], which in turn affect other characteristics such as cohesion and internal friction. Time consolidation may lead to deformations of the particles, effectively enlarging the contact area of particles with their neighbours and the equipment, such that cohesion and adhesion increase [21]. Packing describes the orientation of particles with respect to each other, hence a change in the packing can result in a change of characteristics such as internal friction, bulk density, cohesion, and adhesion. A visualisation of the different mechanical characteristics and the operational conditions is shown in Figure 2.

Methodology

To understand the behaviour of bulk materials, empirical data is required. Therefore, an experimental plan has been developed and shown in Table 1. It specifies the determined mechanical characteristics and the considered operational conditions for each experiment. Using this plan, the behaviour of the fuel and the spent fuel is quantified, such that the gathered data can be used to calibrate, verify, and validate material models in a DEM environment. These models will be used to provide guidelines for the design of storage and handling equipment.

Discussion

Ring shear tests, sieve analysis and imaging, but also individual particle strength tests showed that $NaBH_4$ is a free flowing material, unless it is consolidated over time or the moisture content exceeds a certain level. Furthermore, dynamic vapour sorption tests indicated a threshold for the relative humidity of the environment above which $NaBH_4$ starts to attract water from the air. Surprisingly, this threshold differs from the 19% RH found in the work of Murtomaa [22], Li [23], and Beaird [24]. Lastly, once moisture has been absorbed by $NaBH_4$, it could not simply be removed by drying the material, as the material would cake together and form a single large

Experiment	Mechanical Characteristics	Operational Conditions
Ring Shear Tester	• Bulk Density • Cohesion • Internal Friction • Tensile Strength • Unconfined Yield Stress • Consolidation Stress • Flow Function • Lateral Stress Ratio • Wall Friction • Adhesion	• Time Consolidation • Handling • Temperature[1] • Relative Humidity[1]
Sieve	• Particle Size (Distribution)	• Time Consolidation • Handling
Imaging	• Particle Size (Distribution) • Particle Shape (Distribution)	-
Individual Particle Strength Test	• Particle Strength	-
Dynamic Vapour Sorption Test	• Moisture Uptake[2]	• Relative Humidity
Moisture Depth Test	• Moisture Penetration (Rate)[2]	• Handling
Ledge Test	• Angle of Repose	• Time Consolidation • Temperature[1] • Relative Humidity[1]
Draw Down Test	• Angle of Repose • Shear Angle • Discharging Time	• Time Consolidation • Temperature[1] • Relative Humidity[1]
Equipment Test[3]	• T.B.D.	• T.B.D.

Table 1: Determined Mechanical Characteristics with Experiments

1: Depends upon the availability of a climate chamber
2: Moisture is not a mechanical characteristic, but it greatly affects them and is categorised as such
3: An experiment with real-life equipment is required to validate the developed DEM models

mass. These first results indicate that handling and storage equipment for $NaBH_4$ has to be designed such that no moisture can be absorbed by the material, but how time consolidation will affect the design is not yet clear.

Conclusions

$NaBH_4$ holds great promise as an alternative fuel for the maritime industry, and a circular bunkering process has been proposed which shows the required storage and handling equipment for both port and vessel operations. As the design of storage and handling equipment strongly depends on the mechanical characteristics of the fuel and the spent fuel, which are currently unknown, an experimental plan has been proposed to determine the relevant mechanical characteristics under various operational conditions. Preliminary results showed that an increase in moisture content in combination with time consolidation alters their behaviour indicating the importance of taking into account the storage and handling conditions on the vessel and at the port. DEM simulations are expected to provide insight into the behaviour of the materials, such that efficient equipment can be designed and $NaBH_4$ can be used as fuel for maritime vessels.

This research is supported by the project Sustainable Hydrogen Integrated Propulsion Drives (SH2IPDRIVE), which has received funding from RvO (reference number MOB21013), through the RDM regulation of the Ministry of Economic Affairs and Climate Policy.

References

[1] *Taking the lead on climate change*. URL: https://www.consilium.europa.eu/en/eu-climate-change/ (visited on 11/18/2022).

[2] *Klimaschutz report 2020*. 2020. URL: www.bdl.aero/wp-content/uploads/2021/03/klimaschutzreport2020_final-1.pdf (visited on 11/18/2022).

[3] *IMO's work to cut GHG emissions from ships*. URL: https://www.imo.org/en/MediaCentre/HotTopics/Pages/Cutting-GHG-emissions.aspx (visited on 11/18/2022).

[4] Birudula Anil Kumar et al. "A Coordinated Control Strategy for a Diesel-Electric Tugboat System for Improved Fuel Economy". In: *IEEE Transactions on Industry Applications* 56.5 (Sept. 2020). Conference Name: IEEE Transactions on Industry Applications, pp. 5439–5451. ISSN: 1939-9367. DOI: 10.1109/TIA.2020.3010779.

[5] M.C. van Benten, N. Kougiatsos, and V. Reppa. "Mission-oriented Modular Control of Retrofittable Marine Power Plants: 16th International Naval Engineering Conference and Exhibition incorporating the International Ship Control Systems Symposium, INEC/iSCSS 2022". In: *Proceedings of the International Ship Control Systems Symposium* 16.20 (2022). ISSN: 2631-8741. DOI: 10.24868/10721.

[6] O.B. Inal, J.F. Charpentier, and C. Deniz. "Hybrid power and propulsion systems for ships: Current status and future challenges". In: *Renewable and Sustainable Energy Reviews* 156 (Mar. 2022), p. 111965. ISSN: 1364-0321. DOI: 10.1016/j.rser.2021.111965. URL: https://www.sciencedirect.com/science/article/pii/S1364032121012302.

[7] E. van Rheenen et al. *A review of the potential of hydrogen carriers for zero emission, low signature ship propulsion systems*. preprint. Meeting Name: International Naval Engineering Conference. Oct. 2022. DOI: 10.24868/10649. URL: https://library.imarest.org/record/10649.

[8] Ç. Çakanyildirim and M. Gürü. "The Production of $NaBH_4$ from Its Elements by Mechanochemical Reaction and Usage in Hydrogen Recycle". In: *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* 33.20 (July 2011), pp. 1912–1920. ISSN: 1556-7036, 1556-7230. DOI: 10.1080/15567030903503175. URL: http://www.tandfonline.com/doi/abs/10.1080/15567030903503175.

[9] Y. Nagar et al. "Modeling the mechanical behavior of sodium borohydride ($NaBH_4$) powder". In: *Materials & Design* 108 (Oct. 2016), pp. 240–249. ISSN: 02641275. DOI: 10.1016/j.matdes.2016.06.077. URL: https://linkinghub.elsevier.com/retrieve/pii/S0264127516308334.

[10] P. Brack, S.E. Dann, and K.G.U Wijayantha. "Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride ($NaBH_4$) solutions". In: *Energy Science & Engineering* 3.3 (May 2015), pp. 174–188. ISSN: 20500505. DOI: 10.1002/ese3.67. URL: https://onlinelibrary.wiley.com/doi/10.1002/ese3.67.

[11] D. Lensing. "A study on the integration of a novel NaBH4 fuelled hybrid system for a small inland vessel". Apr. 2020.

[12] F.M. Nievelt. "Maritime application of sodium borohydride asan energy carrier". Feb. 2019.

[13] A. Düll et al. “Performance Evaluation of KBH $_4$ as Energy Carrier for Shipping Applications”. In: *Chemie Ingenieur Technik* 94.5 (May 2022), pp. 747–759. ISSN: 0009-286X, 1522-2640. DOI: 10.1002/cite.202100193. URL: https://onlinelibrary.wiley.com/doi/10.1002/cite.202100193.

[14] Y. Zhu et al. “Closing the Loop for Hydrogen Storage: Facile Regeneration of NaBH $_4$ from its Hydrolytic Product”. In: *Angewandte Chemie* 132.22 (May 2020), pp. 8701–8707. ISSN: 0044-8249, 1521-3757. DOI: 10.1002/ange.201915988. URL: https://onlinelibrary.wiley.com/doi/10.1002/ange.201915988.

[15] W. Chen et al. “Hydrolysis and regeneration of sodium borohydride (NaBH4) – A combination of hydrogen production and storage”. In: *Journal of Power Sources* 359 (Aug. 2017), pp. 400–407. ISSN: 0378-7753. DOI: 10.1016/j.jpowsour.2017.05.075. URL: https://www.sciencedirect.com/science/article/pii/S0378775317307267 (visited on 10/02/2023).

[16] H.X. Nunes et al. “Rehydrogenation of Sodium Borates to Close the NaBH4-H2 Cycle: A Review”. In: *Energies* 14.12 (Jan. 2021). Number: 12 Publisher: Multidisciplinary Digital Publishing Institute, p. 3567. ISSN: 1996-1073. DOI: 10.3390/en14123567. URL: https://www.mdpi.com/1996-1073/14/12/3567.

[17] M.C. van Benten, J.T. Padding, and D.L. Schott. “Towards Hydrogen-Fuelled Marine Vessels using Solid Hydrogen Carriers”. In: *The 14th International Conference on Bulk Materials Storage, Handling and Transportation*. Wollongong, Australia, July 2023.

[18] D. Schulze. *Powders and bulk solids: behavior, characterization, storage and flow*. OCLC: ocn166372537. Berlin ; New York: Springer, 2008. ISBN: 978-3-540-73767-4.

[19] Zhigang Cao et al. “Thermal Effects on Shear Characteristics of Unbound Granular Materials under Drained Conditions”. In: *Journal of Geotechnical and Geoenvironmental Engineering* 149.4 (Apr. 2023). Publisher: American Society of Civil Engineers, p. 04023012. DOI: 10.1061/JGGEFK.GTENG-10803. URL: https://ascelibrary.org/doi/10.1061/JGGEFK.GTENG-10803 (visited on 06/21/2023).

[20] H Kalman. “Particle Breakage and Attrition”. In: *KONA Powder and Particle Journal* 18 (2000), pp. 108–120. DOI: 10.14356/kona.2000017.

[21] Mingyang Chen et al. “Amorphous and humidity caking: A review”. In: *Chinese Journal of Chemical Engineering* 27.6 (June 2019), pp. 1429–1438. ISSN: 10049541. DOI: 10.1016/j.cjche.2019.02.004. URL: https://linkinghub.elsevier.com/retrieve/pii/S1004954118308747.

[22] M. Murtomaa et al. “On effects of ambient humidity on sodium borohydride powder”. In: *Powder handling & processing* Vol. 11.No. 1 (Jan. 1999).

[23] P. Li et al. “Deliquescence of NaBH4 from Density Functional Theory and Experiments”. In: *Industrial & Engineering Chemistry Research* 52.38 (Sept. 2013). Publisher: American Chemical Society, pp. 13849–13861. ISSN: 0888-5885. DOI: 10.1021/ie401742u. URL: https://doi.org/10.1021/ie401742u.

[24] A.M. Beaird, T.A. Davis, and M.A. Matthews. “Deliquescence in the Hydrolysis of Sodium Borohydride by Water Vapor”. In: *Industrial & Engineering Chemistry Research* 49.20 (Oct. 2010). Publisher: American Chemical Society, pp. 9596–9599. ISSN: 0888-5885. DOI: 10.1021/ie100244v. URL: https://doi.org/10.1021/ie100244v.