Circular bunkering for maritime vessels using sodium borohydride

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

DOI
10.1016/j.rser.2025.116039

Publication date
2025

Document Version
Final published version

Published in
Renewable and Sustainable Energy Reviews

Renewable and Sustainable Energy Reviews 223 (2025) 116039

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Circular bunkering for maritime vessels using sodium borohydride

M.C. van Benten [a,*], J.T. Padding [b], D.L. Schott [a]

[a] Maritime and Transport Technology, Delft University of Technology, Mekelweg 2, 2628CD, Delft, the Netherlands
[b] Process and Energy, Delft University of Technology, Leeghwaterstraat 39, 2628CB, Delft, the Netherlands

HIGHLIGHTS

- Mechanical characteristics of $NaBH_4$ are fundamental to bunkering system design.
- The effect of operational conditions on $NaBH_4$ must be experimentally studied.
- Better understanding of the flow behaviour of $NaBH_4$ is critical for safe fuel handling.
- Circular bunkering system design must include both $NaBH_4$ and its spent fuel.
- Circular $NaBH_4$ bunkering requires adaptations to current port and vessel infrastructure.

ARTICLE INFO

Keywords:
Sodium borohydride
Sodium metaborate
Hydrogen carriers
Circular bunkering
Granular fuels
Mechanical characteristics
Operational conditions
Maritime shipping

ABSTRACT

To reduce global emissions, hydrogen is increasingly considered as an energy carrier for renewable energy storage. However, traditional storage methods for hydrogen such as compression or liquefaction require high pressures, extremely low temperatures, and still result in a low volumetric energy density. As a solution, sodium borohydride ($NaBH_4$) is proposed as an alternative method to store hydrogen. $NaBH_4$ is a granular material that can be stored using ambient temperature and pressure, and has a relatively high volumetric and gravimetric energy density compared to traditional hydrogen storage. This paper explores the application of $NaBH_4$ as a fuel in the maritime industry, and elaborates on how the use of $NaBH_4$ leads to a circular bunkering (refuelling) process. By using hydrolysis to extract hydrogen from $NaBH_4$ during vessel operation, a so called spent fuel remains and needs to be stored on the vessel until next port call. Additionally, examples of various bunkering equipment that can be used to design the circular bunkering process of $NaBH_4$ are presented. Moreover, it explains how design of bunkering equipment depends on the mechanical characteristics of the fuel and spent fuel. The main finding of this work is that $NaBH_4$ is a promising solution for a sustainable future. Before $NaBH_4$ can be used as a fuel, vessels and ports need to be adapted to facilitate circular bunkering with such a novel solid-state energy carrier.

1. Introduction

Greenhouse gas emissions drive global warming [1], which could cause considerable and permanent damage to natural ecosystems and human societies. Therefore, at the Paris Climate Conference in 2015, an agreement was reached to implement measures to restrict global warming to a maximum of 2 °C [2]. Given that the maritime sector contributes around 3 % of global emissions, with a projected increase [3], the International Maritime Organisation (IMO) has set targets to reduce maritime emissions by at least 50 % by 2050, relative to 2008 levels [4]. One strategy to achieve these targets is for marine vessels to adopt alternative fuels, such as hydrogen [5,6]. Traditionally, hydrogen is stored through compression [7,8], but also liquefaction, or cryocompression (liquefaction under high pressure), which is well described in literature. However, these storage methods encounter issues like high pressure, low volumetric density, high energy consumption, and the necessity for thick insulated walls.

To overcome these disadvantages, alternative methods to store hydrogen are increasingly researched, and an overview of these methods is shown in Fig. 1, inspired by the work of van Rheenen et al. [9]. These alternative storage methods can be sorted into two categories: liquid and solid.

Liquid hydrogen carriers can be broadly categorised into silane-based, nitrogen-based, and organic compounds. Silane-based carriers

* Corresponding author.
Email address: m.c.vanbenten@tudelft.nl (M.C. van Benten).

https://doi.org/10.1016/j.rser.2025.116039
Received 5 November 2024; Received in revised form 12 June 2025; Accepted 30 June 2025
Available online 10 July 2025

Nomenclature

Abbreviations

DBT Dibenzyltoluene
H_2 Hydrogen
H_2O Water
IMO International Maritime Organization
KBH_4 Potassium borohydride
LHV Lower Heating Value
$LiBH_4$ Lithium borohydride
LiH Lithium hydride
LNG Liquid Natural Gas
LOHC Liquid Organic Hydrogen Carrier
Mg Magnesium
MgH_2 Magnesium hydride
MgO Magnesium oxide
MOF Metal Organic Framework
$NaBH_4$ Sodium borohydride
$NaBO_2$ Anhydrous sodium metaborate
$NaBO_2{\cdot}2H_2O$ Dihydrate sodium metaborate
$NaBO_2{\cdot}4H_2O$ Tetrahydrate sodium metaborate
NH_3 Ammonia
NH_3BH_3 Ammoniaborane
PHS Polyhydrosiloxane
PTS Port-to-Ship or Pipe-to-Ship
RH Relative Humidity
Si_5H_{12} Pentasilane
SiH_4 Silane gas
STS Ship-to-Ship
TEU Twenty-foot Equivalent Unit
TTS Truck-to-Ship
wt% Weight percent

Symbol

A Area [m^2]
c Clearance [m]
D Diameter [m]
f Friction factor [–]
g Gravitational acceleration [m/s^2]
K Lateral stress ratio [–]
L Length [m]
m Mass [kg]
M Molar mass [g/mol]
n Rotational speed [rpm]
P Pressure [Pa]
p Pitch [m]
t Thickness [m]
T Temperature [K]
U Circumference [m]
V Volume [m^3]
z Height [m]
$\dot{Q}$ Flow rate [m^3/s]
ρ Density [kg/m^3]
σ Stress [Pa]
η Efficiency [–]
°C Degrees Celsius [°C]

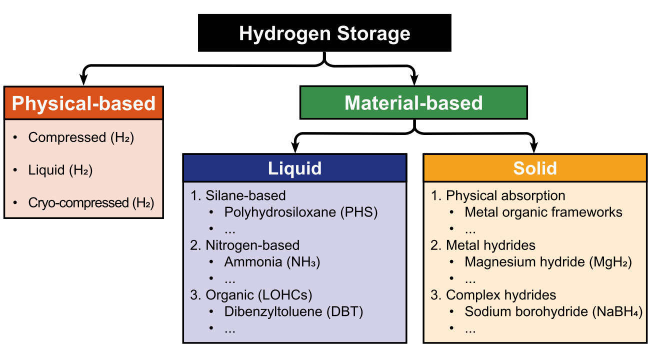

Fig. 1. Classification of hydrogen storage methods.

consist of silicon and hydrogen compounds that react with water in the presence of catalysts to release hydrogen and form silicon dioxide. Among these, silane gas (SiH_4) has a high storage capacity but is highly flammable. Safer alternatives such as polyhydrosiloxane (PHS) and pentasilane (Si_5H_{12}) have been proposed, but their storage capacity is significantly less than that of silane gas [10]. Nitrogen-based storage options are primarily represented by ammonia, which has a high hydrogen content, but to remain liquid, it requires low temperatures or elevated pressure [11]. Furthermore, ammonia is highly toxic and corrosive [11], and the release of hydrogen is endothermic and requires high temperatures [12]. Organic carriers, commonly referred to as liquid organic hydrogen carriers (LOHCs), are generally safe and easy to handle. Despite these advantages, they suffer from relatively low hydrogen storage capacities, and hydrogen release is an endothermic process that typically requires high temperatures [12,13].

Solid hydrogen carriers can be broadly classified into three categories: physical absorption, metal hydrides, and complex hydrides. Each class presents distinct advantages and limitations in terms of hydrogen storage, reversibility, and operational conditions. Physical absorption materials, such as metal-organic frameworks (MOFs), store hydrogen within their porous structures without breaking the H-H bond [14,15]. While these materials offer reversible storage, their storage capacities significantly degrade over multiple cycles [7], and they typically require low temperatures and high pressures to maintain sufficient hydrogen storage capacities [16–18]. Metal hydrides, such as lithium hydride (LiH) and magnesium hydride (MgH_2), chemically bind hydrogen within their crystal structure. LiH offers a relatively high storage capacity but is highly reactive with water and requires high temperatures for hydrogen release [19–21]. MgH_2 is more stable, and also easier and safer to handle, though it also requires high temperatures for hydrogen release, and it has lower storage capacity than LiH [21,22].

Complex hydrides consist of boranes and borohydrides: molecules that either have a BH_3 or BH_4 group [23]. Among boranes, ammonia borane (NH_3BH_3) has attracted significant attention due to its high hydrogen content. Hydrogen can be released from ammonia borane through pyrolysis, alcoholysis, or hydrolysis, with the latter being the most favourable due to its relatively mild operating conditions [24]. For hydrolysis, ammonia borane reacts with water to produce hydrogen, ammonia, and borates [25]. However, a key limitation is that not all stored hydrogen is released during the reaction, reducing its effective storage capacity [26,27].

Common borohydrides are lithium borohydride ($LiBH_4$), sodium borohydride ($NaBH_4$), and potassium borohydride (KBH_4) [9]. All three can release hydrogen through pyrolysis or hydrolysis. Pyrolysis generally requires high temperatures, making hydrolysis the more favourable technique. $LiBH_4$ has the highest storage capacity but shows less efficient hydrolysis. This leaves KBH_4 and $NaBH_4$, and since the latter has a higher storage capacity than the former [9], $NaBH_4$ is a much-researched borohydride for hydrogen storage.

$NaBH_4$ is a granular material that is traditionally used as a reducing agent in the chemical industry [28–33]. Using $NaBH_4$ offers several significant benefits: it is non-flammable, can be stored under ambient conditions, and has a relatively high energy density [34–36]. In terms of both gravimetric and energy density, $NaBH_4$ is expected to outperform compressed hydrogen by a factor of four to six, due to its ability to store a higher amount of hydrogen [37]. While physical hydrogen storage methods typically provide pure hydrogen by simply opening a few valves, releasing hydrogen from material-based storage systems requires more effort. For $NaBH_4$, hydrogen can be liberated through two main processes: thermolysis or hydrolysis. Thermolysis is less favourable as it necessitates high temperatures, between 400 °C and 600 °C [38–40]. To reduce the high-temperature requirements of thermolysis, Mao et al. [41] studied the effects of additives on the decomposition temperature of several $NaBH_4$-additive mixtures. They concluded that they could lower the thermal requirements for thermolysis, but it is still too high for practical applications. Kumar et al. [42] investigated a similar approach and managed to reduce the decomposition temperature to well below 300 °C, but this is still considerably high. In contrast, hydrolysis can occur under ambient conditions, as borohydrides react spontaneously and exothermically with water [19,43] and can be accelerated with catalysts such as ruthenium, platinum, or cobalt [44,45].

Due to these advantages, using sodium borohydride as a fuel is being researched increasingly. Aiello et al. [46], Marrero-Alfonso et al. [47], Senoh et al. [48], Marchionni et al. [49], Xueping et al. [50], Chen et al. [51], Lee et al. [45], and Jeong et al. [52] focus on the hydrolysis reaction, but Gislon et al. [53] also include the hydrolysis reactor design. Alligier et al. [54] and Arzac et al. [55] focus on the hydrolysis of $NaBH_4$ in combination with fuel cells. Luo et al. [56], Ma et al. [57], and Miley et al. [58] study the use of a direct borohydride fuel cell, avoiding the need for a separate hydrolysis reaction. Mohring and Luzader [59] investigate and present the design of a sodium borohydride power plant for road vehicles and report successful implementation. They use hydrolysis to release the hydrogen, which they then feed to either fuel cells or combustion engines. Kim et al. [60] and Kwon et al. [61] present the design of a power plant for an unmanned aerial vehicle using $NaBH_4$, employing hydrolysis and fuel cells. They also manufactured the proposed design and documented successful operation. Santos and Sequeira [62] conducted a thorough literature study on the application of sodium borohydride as a fuel, and Rivarolo et al. [63] investigated the techno-economic aspects of the use of sodium borohydride for hydrogen storage. The use of sodium borohydride on maritime vessels is investigated by Lensing [64], and also the Indian navy showed interest in the use of $NaBH_4$ for its submarines [65,66].

It has to be noted that many authors describe a mixture of sodium borohydride and water as fuel, which greatly reduces the energy density. Only Kwon et al. [61] use solid-state $NaBH_4$ in their designs, and Lensing [64] describes both solutions and solid-state $NaBH_4$. Furthermore, besides the work of Nievelt [67], the required handling and storage steps are not mentioned, which are crucial when considering a novel fuel for any type of application. Broadening the scope to derivatives of $NaBH_4$, Düll et al. [68] describe the use of KBH_4 on maritime vessels. They mention solid-state storage of the fuel but do not describe the handling and storage steps.

The novelty of this work lies in the development of a circular bunkering process for sodium borohydride as a solid fuel for maritime vessels. While previous studies have focused primarily on the reaction kinetics, fuel cell integration, system-level applications, or techno-economic aspects of $NaBH_4$, they rarely address the practical applications of using $NaBH_4$ as a solid-state, granular fuel in maritime operations. In contrast, this study identifies the adaptations and innovations required for existing ports and vessels to utilise $NaBH_4$, considering both the fuel and the spent fuel. It is also amongst the few that consider the implications of the rather chemically-oriented working principles of sodium borohydride as a fuel on the design of the storage and handling equipment that is required. Therefore, this study first discusses the state-of-the-art bunkering processes of traditional fuels in the maritime industry in order to identify the required handling and storage steps. Then, it demonstrates how these processes must change when switching to $NaBH_4$ as a fuel and finally outlines the different requirements for the equipment onboard vessels and at ports, together with the required mechanical characteristics of solid-state $NaBH_4$.

2. Bunkering of maritime vessels

The state-of-the-art bunkering methods for maritime vessels are derived using the Port of Rotterdam and the Port of Amsterdam as examples [69–72], and three different bunkering methods are used to supply maritime vessels with fuel are identified:

- Ship-to-Ship (STS)
- Port-to-Ship or Pipe-to-Ship (PTS)
- Truck-to-Ship (TTS)

Ship-to-Ship bunkering means that a specialised refuelling vessel, vessel A, is used to supply fuel to the vessel in need, vessel B (also referred to as mother and daughter vessels, respectively [73]). This can be either in the port, close to the port, or on the open ocean. Truck-to-Ship bunkering entails the refuelling of vessel B by means of trucks alongside the quay, and for Port-to-Ship bunkering, vessel B connects to a fixed refuelling point in the harbour. Often the fuel supplied through these refuelling points is stored in the port, e.g., the Port of Amsterdam has a fuel supply that stores up to nine times the daily fuel demand, as reported by Roos [74]. However, as the fuel that is supplied to the vessel when connected to the fixed refuelling point can also be stored elsewhere, this is also referred to as Pipe-to-Ship. The bunkering methods are summarised in Fig. 2.

Furthermore, Liquid Natural Gas (LNG) is more and more adapted in ports worldwide and readily available as a bunkering fuel through either of the three bunkering methods described [75–77]. Next to that, ammonia and hydrogen are also considered as alternative fuels and are likely to be bunkered using STS, TTS, or PTS [78–81].

Although the presented (one-way) bunkering methods prove useful and are well used for conventional fuels and increasingly for alternative fuels, the use of $NaBH_4$ as a fuel requires several adaptations to the fuel infrastructure of both the ports and the vessels such that a circular bunkering process is realised. What this means, and how this works, will be discussed in the next section.

3. Circular bunkering process

While conventional fuels only produce exhaust gases during vessel operation, using sodium borohydride on board marine vessels requires a circular bunkering process where next to fuel, spent fuel is stored. Inspired by the work of Düll et al. [68], who investigated the use of

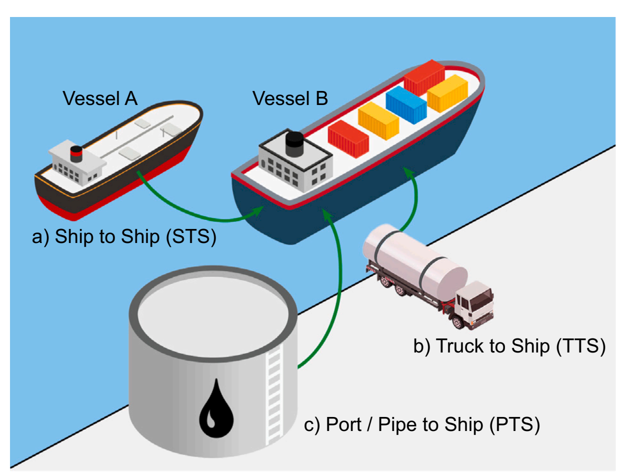

Fig. 2. Traditional bunkering of (alternative) fuels.

potassium borohydride as fuel for marine vessels from a chemical point of view, the circular bunkering process for a single vessel using sodium borohydride ($NaBH_4$) is illustrated in Fig. 3. First, the sodium borohydride, acting as the fuel, is stored at the port fuel storage facility. From here, it can be transferred to the vessel's onboard fuel tanks when the vessel is moored at the quay. During vessel operation, the $NaBH_4$ must be continuously mixed with purified seawater (fuel preparation) before being fed into the chemical reactor. Here, hydrogen can be released via the hydrolysis of $NaBH_4$, as shown in Eq. (1) [82,83]. This reaction produces (after a crystallisation step) dry or hydrated sodium metaborate ($NaBO_2 \cdot xH_2O$) as a by-product, commonly referred to as spent fuel.

$$NaBH_4 + (2 + x)H_2O \rightarrow NaBO_2 \cdot xH_2O + 4H_2 \quad (1)$$

Here, $x \in [0, 2, 4]$ is the degree of hydration of the spent fuel crystals. Typically, a higher degree of hydrogenation increases the efficiency of the reaction. The obtained hydrogen can be used in, e.g., fuel cells to generate the required propulsion and auxiliary power for the vessel, and the sodium metaborate ($NaBO_2 \cdot xH_2O$) has to be stored until the next port call. The sodium metaborate, called spent fuel, is separated from the unreacted fuel and water by crystallisation in the spent fuel treatment and subsequently stored in the spent fuel storage tanks. Note that the unreacted fuel is fed back into the reactor.

Upon arrival at the destination port, the vessel receives new fuel ($NaBH_4$), while simultaneously the spent fuel can be retrieved from these tanks and transported to the regeneration facility, where first the spent fuel is prepared for the primary regeneration step. Then, one of the following reactions occurs [34,84,85]:

$$NaBO_2 + 2MgH_2 \rightarrow NaBH_4 + 2MgO \quad (2)$$

$$NaBO_2 \cdot xH_2O + yMg \rightarrow NaBH_4 + (2 + x)MgO + (x - 2)H_2 \quad (3)$$

where $x \in [2, 4]$. Mg stands for magnesium (pure), MgH_2 for magnesium hydride (both referred to as reductive agents), and MgO denotes magnesium oxide. The obtained $NaBH_4$ has to be separated from the unconverted spent fuel and magnesium oxide and subsequently dried. Finally, the magnesium oxide can be regenerated into the required reductive agent using pure hydrogen in the secondary regeneration. Whether the process can be described by Eq. (2) or Eq. (3) depends on the excess water used in the chemical reactor and if the spent fuel is dried to $NaBO_2$ on board the vessel. As the latter requires temperatures up to 250 °C, an alternative is to store the hydrated ($NaBO_2{\cdot}2H_2O$ or $NaBO_2{\cdot}4H_2O$) spent fuel, which has the benefit that only magnesium is required for the regeneration. Even more, in the case of $NaBO_2{\cdot}4H_2O$, hydrogen is produced in the regeneration. The downside of the hydrated spent fuels is that they have a higher molar volume and mass, which can be more challenging to incorporate into vessel design. This increase in mass and volume originates from the addition of external water in Eq. (1) in twofold. First, four hydrogen atoms are replaced by two oxygen atoms, increasing the molecular mass. Second, any excess of water is retained in the spent fuel as crystal water, further contributing to both mass and volume. This results in a different molar mass and volume for the fuel and the three possible forms of spent fuel, and these are listed in Table 1. Note that each mole of $NaBH_4$ results in a mole of the spent fuel. Therefore, the total weight of each generated spent fuel (whether anhydrous, dihydrate, or tetrahydrate) is more than that of the original fuel. However, storing the anhydrous spent fuel reduces the required storage volume compared to the dihydrate and tetrahydrate spent fuel. This means that regardless of the type of spent fuel, the vessel will increase in mass during its voyage, but the exact amount of mass increase can be regulated using the amount of drying of the spent fuel. The exact operating principles of the chemical reactor and the regeneration facility are still being researched [16,86], and also the design of the bunkering process can affect these processes, and vice versa. As a result, it is not yet known which spent fuel will have to be stored on the vessel and in the port. Still, we do know for certain that we need to bunker sodium borohydride and one of the three forms of sodium metaborate. Consequently, we can already give directions for the design of the required bunker process.

Table 1
Molar volume and mass of sodium borohydride and sodium metaborate (https://pubchem.ncbi.nlm.nih.gov; https://www.borax.com).

	Particle density [g/L]	Molar volume [mL/mol]	Molas mass [g/mol]
$NaBH_4$	1.07	35.36	37.84
$NaBO_2$	2.46	26.70	65.80
$NaBO_2 \cdot 2H_2O$	1.90	53.59	101.83
$NaBO_2 \cdot 4H_2O$	1.74	79.23	137.86

Using the traditional bunkering practices depicted in Fig. 2 and the requirements for using sodium borohydride as a marine fuel shown in Fig. 3, the required circular bunkering process can be deduced. Unlike traditional methods, which only require the transfer of fuel from the storage facility to the vessel, the use of $NaBH_4$ as a marine fuel introduces the retrieval of spent fuel from vessels back to the storage facilities, as depicted in Fig. 4. Note that the bunkering methods do not change in definition, but an additional backflow of spent fuel is only added. This implies that the existing infrastructure for bunkering marine vessels has to be expanded significantly. Furthermore, since the fuel and spent fuel are not liquids, but granular materials, the equipment needs to be adjusted accordingly. Even more, as granular materials can be sensitive to operational conditions, such as (ambient) temperature and humidity

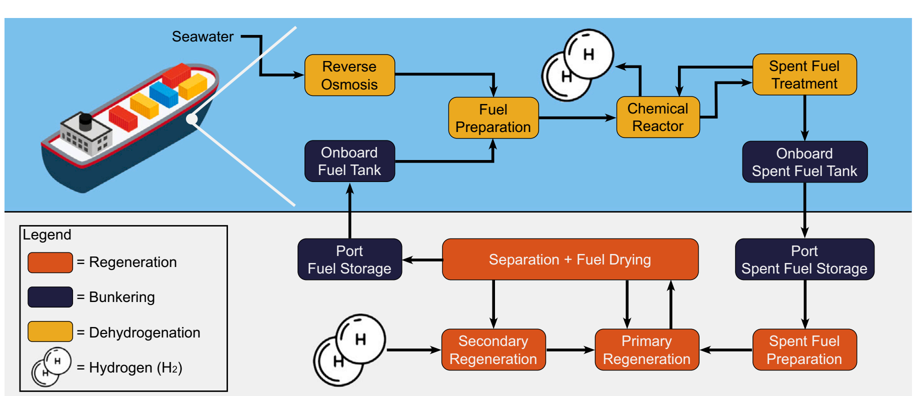

Fig. 3. Sodium borohydride and sodium metaborate as marine fuel. Note: generating power with hydrogen produces water, which is reused by the fuel preparation and the hydrolysis reaction, but this is not shown here to avoid complexity.

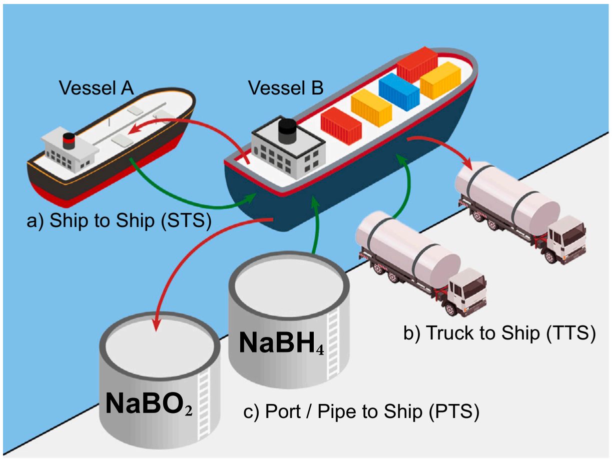

Fig. 4. Circular bunkering of sodium borohydride and sodium metaborate.

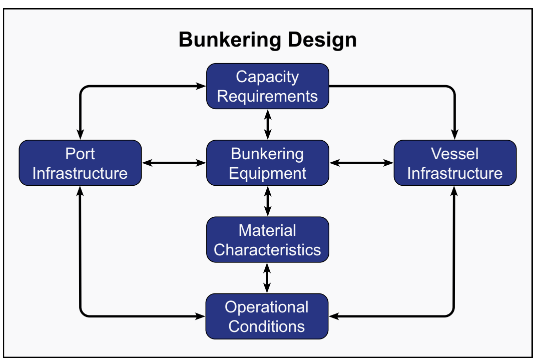

Fig. 5. Design elements for bunkering design.

[87–89], this has to be taken into account when designing the circular process. These different design elements affecting the bunkering design are summarised in Fig. 5, and need to be evaluated before this novel circular bunkering process can be implemented in ports and vessels (arrows indicate the connections between the design elements).

4. Port infrastructure

It is evident from Fig. 4 that modifications to the port infrastructure are necessary before sodium borohydride can be used as fuel for marine vessels. First, regardless of the bunkering method, the equipment has to be suitable for transporting granular materials instead of fluids and gases. Furthermore, for PTS bunkering, alongside the fuel being provided to the vessel, the spent fuel has to be reclaimed and stored, introducing additional equipment for the transportation and storage of the spent fuel to the port's infrastructure. TTS bunkering increases the number of truck movements to, from, and within the port. Only for STS bunkering the infrastructure of the refuelling port might remain unchanged, although the lower energy density of $NaBH_4$, compared to traditional fuels, increases either the size or the number of required refuelling ships. In summary, the above-stated modifications effectively double the handling and transport operations, potentially creating logistical challenges. Additionally, an on-site regeneration plant may be needed, which could also handle spent fuel from other ports. The regenerated fuel would then need to be redistributed, creating multiple streams of granular materials to, from, and within the ports.

4.1. Capacity requirements

To gain insight into the port requirements concerning the bunkering of sodium borohydride, a comparative analysis with conventional bunker fuel and $NaBH_4$ is conducted. Typically, energy densities are compared to draw conclusions; however, given that the circular bunkering system illustrated in Fig. 4 is not yet fully developed, this task remains complex. Consequently, the analysis in this paper is limited to comparing the chemical energy content of the fuels. Combined with the density of the fuel and spent fuel, this allows for the expression of fuel storage requirements in terms of mass and volume.

Note that the density mentioned above is the bulk density. This is a common term in the field of bulk solids and powder technology, and it captures the granular nature of these materials. While a liquid or a gas can be considered a continuum, granular materials can not. These materials are made up of individual particles, or grains, with air/gas-filled spaces (voids) between them, lowering the overall density of the material. For example, studies that examine the applicability of sodium borohydride for hydrogen storage, e.g., Santos and Sequeira [62] and Li et al. [90], often use its particle density, 1.07 g/cm^3. However, preliminary experiments showed that the bulk density of sodium borohydride is approximately half the particle density, which greatly affects any estimations done on the energy density of systems using this novel fuel. Therefore, in the remainder of the paper, the bulk density will be considered, unless stated otherwise.

The equivalent mass of sodium borohydride is determined using the Lower Heating Value (LHV) of both conventional fuels and hydrogen, together with the mass content of hydrogen in $NaBH_4$. Taking into account that the hydrolysis reaction shown in Eq. (1) effectively doubles the generated hydrogen per unit mass of $NaBH_4$, and that the weight percentage of hydrogen in sodium borohydride is equal to 10.8 %, Eq. (4) can be derived:

$$m_{NaBH_4} = \frac{LHV_{conv.fuel} \cdot m_{conv.fuel}}{LHV_{H_2}} \cdot \frac{1}{2 \cdot wt\%_{H_2}} \quad (4)$$

where m_{NaBH_4} is the equivalent mass of $NaBH_4$, $m_{conv.fuel}$ is the mass of the conventional fuel, $wt\%_{H_2}$ is the weight percentage of hydrogen in $NaBH_4$ (10.8 %) and $LHV_{conv.fuel}$ and LHV_{H_2} are the lower heating values of conventional fuel and hydrogen, respectively. The factor 2 accounts for the hydrogen liberated from the water mixed with the sodium borohydride, in accordance with Eq. (1). As the unreacted $NaBH_4$ is fed back into the reactor, all of the consumed fuel will be converted to spent fuel, assuming a closed system with no losses. This implies that each mole of sodium borohydride is converted to one mole of spent fuel. Therefore, their molar masses (M), provided in Table 1, can be used to convert the storage requirements for sodium borohydride into the corresponding storage requirements for the spent fuel using Eq. (5):

$$m_{spentfuel} = m_{NaBH_4} \cdot \frac{M_{spentfuel}}{M_{NaBH_4}} \quad (5)$$

where M_{NaBH_4} and $M_{spentfuel}$ denote the molar mass of the sodium borohydride and spent fuel, respectively. Finally, the required storage volume (V) for both the sodium borohydride and its spent fuel can be determined using their bulk density (ρ_b), according to Eq. (6):

$$V = \frac{m}{\rho_b} \quad (6)$$

This approach can be used to estimate the required additional storage capacity for ports, by converting each conventional fuel that is bunkered in a port to the equivalent amount of sodium borohydride and its spent fuels. The Port of Rotterdam is taken as a case study. Here, between 7 and 10 million tonnes of fossil fuel are bunkered annually [69]. Table 2 presents the different fossil fuels, quantities bunkered in 2023, and their densities and lower heating values. This is then used to convert the energy contained in these fossil fuels to the amount of sodium borohydride

Table 2
Characteristics of annually bunkered fuels at the port of Rotterdam [91–94].

Fuel	Quantity (2023) [tonnes · 10^5]	Density [kg/m^3]	LHV [MJ/kg]
ULSFO	6.29	850	42.4
VLSFO	27.0	950	41.6
HSFO	24.5	980	40.4
MGO	7.47	850	42.6
MDO	5.06	865	42.7
LNG	2.14	455	48.0

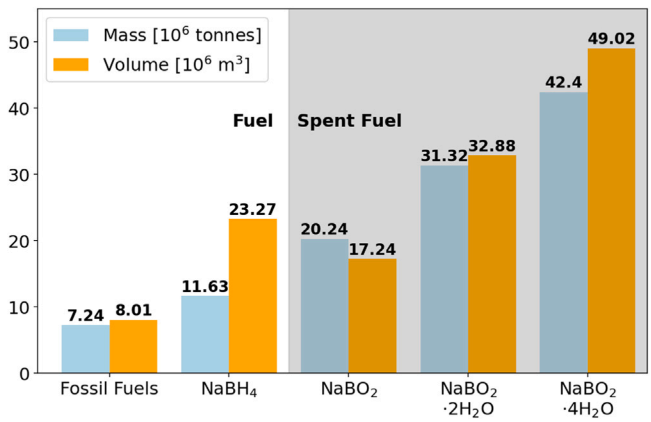

Fig. 6. Port requirements for sodium borohydride with spent fuel compared to fossil fuels. *The bulk density of spent fuel is assumed to be 50 % of their particle density, in line with documented bulk density of 500 kg/m^3 for sodium borohydride (Sigma Aldrich). **The lower heating value of hydrogen is set at 120 MJ/kg.

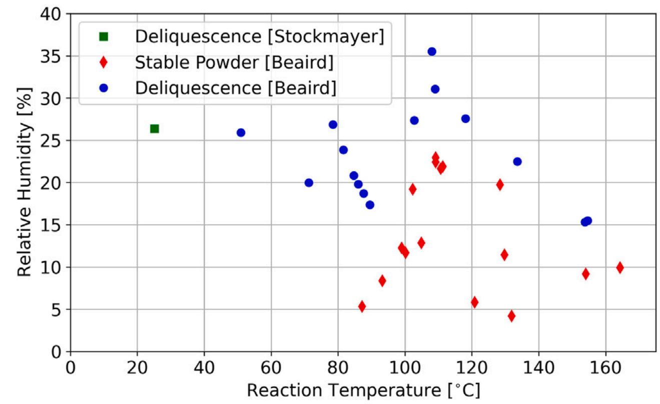

Fig. 7. Deliquescence behaviour of $NaBH_4$ powder as a function of temperature and relative humidity [97,98].

Table 3
Operational conditions of top 10 ports worldwide [101].

Port	Temperature [°C]			Humidity [%RH]		
City/Country	Min	Avg	Max	Min	Avg	Max
Shanghai/China	2	17	32	67	74	81
Singapore/Singapore	25	28	32	78	80	83
Busan/South-Korea	1	15	29	56	69	87
Rotterdam/The Netherlands	2	11	22	73	78	85
Jebel Ali/Dubai	18	30	36	48	56	62
Port Klang/Malaysia	23	28	33	77	81	85
Antwerp/Belgium	2	12	23	71	78	86
Los Angeles/U.S.A	6	22	29	38	50	62
Hamburg/Germany	−1	10	23	73	80	88
Laem Chabang/Thailand	24	28	34	65	74	79

and spent fuel that would be required, and this is shown in Fig. 6. It can be noted that in any case, the mass and volume of the stored $NaBH_4$ are higher than the current practice for fossil fuels. As the spent fuel that will be stored at the port is yet unknown, the increase in storage capacity regarding the spent fuel cannot be predicted with certainty. However, it is evident that mass will increase even more than is the case for the sodium borohydride. Now, although the additional mass and volume that need to be accounted for design of future ports is an important aspect, the operational conditions while handling and storing the fuel and spent fuel must also be considered.

4.2. Hygroscopic behaviour of $NaBH_4$

Next to the storage capacity requirements for the bunkering of sodium borohydride, understanding the operational conditions for port equipment is crucial for efficient and safe bunkering operations. Since sodium borohydride and its spent fuels are granular materials, their behaviour is affected by operational conditions such as temperature and humidity [95]. More importantly, sodium borohydride is hygroscopic and absorbs moisture from the ambient air if no countermeasures are taken [96].

Murtomaa et al. [96] investigated the effect of relative humidity on the absorption of moisture and found that the powder was stable up to 19 %RH at 25 °C. Furthermore, the rate at which moisture was absorbed increased with increasing humidity with an initial high absorption rate that gradually stabilised over time. This can be explained by the formation of dihydrates ($NaBH_4 \cdot 2H_2O$). Initially, the sodium borohydride crystal absorbs the moisture from the air to form a dihydrate.

As the dihydrate can not take up any more water, the crystal begins to dissolve. The dissolution is slower than the formation of dihydrates, hence the gradually decreasing moisture absorption rate. Furthermore, Beaird et al. [98] state that $NaBH_4$ attracts moisture until it is completely dissolved, a phenomenon known as deliquescence. They also investigated the specific conditions that were required for deliquescence and found that for certain combinations of temperature and relative humidity, the crystals did not attract any moisture from the ambient air, but outside of this 'safe' region, deliquescence occurred. They compared their results with the work of Stockmayer et al. [97] and found a good agreement. The results are shown in Fig. 7. Their findings are also in line with the (previously described) work of Murtomaa et al. [96]. Additionally, no hydrogen release was measured during the moisture uptake by $NaBH_4$ when studying the deliquescence, which is also confirmed by Kong et al. [99]. Fillinchuk and Hageman [100] and Murtomaa et al. investigated the stability of the dihydrate crystals. They found that once formed, $NaBH_4 \cdot 2H_2O$ decomposes at temperatures exceeding 40 °C, releasing the water that was initially absorbed. When further heated, Fillinchuck and Hagemann observed that hydrogen was released by the reaction of $NaBH_4$ and H_2O. Therefore, it can be concluded that although the deliquescent behaviour of sodium borohydride causes the formation of dihydrates and eventually leads to the complete dissolving of the initial dry material, no hydrogen is generated unless it is heated.

4.3. Operational conditions and design implications

Now, assuming that the bunkering process for sodium borohydride will occur at one or more of the world's largest ports and knowing that the deliquescent behaviour of $NaBH_4$ is affected by temperature and relative humidity, the environmental conditions at these locations should be considered. Table 3 provides a summary of the temperatures and relative humidity at the ten largest ports, which can influence the design requirements for port equipment handling sodium borohydride.

It is evident that for each of the ports depicted in the table, the minimum relative humidity exceeds the deliquescence limits of $NaBH_4$.

Therefore, unless countermeasures are implemented to isolate the material from ambient air—such as using closed, actively controlled storage and transport systems to ensure the relative humidity is sufficiently low—deliquescence will occur, effectively resolving the fuel and transforming it from a granular solid to a liquid. This is highly undesired, as this decreases the energy density of the circular bunkering process significantly and could damage the storage and handling equipment. Therefore, the next section will describe the requirements for the bunkering process at ports.

4.4. Bunkering requirements

Limited research has been found regarding such a novel, circular bunkering process, and therefore a quantitative review and comparison of the exact equipment requirements can not yet be provided. Fortunately, the use of granular materials as fuel for maritime vessels is not a novel concept, as historically, steamships relied on coal as an energy supply [102]. Next to that, handling and storing granular materials has been done for decades [103]. Common dry bulk materials as commodities are iron ore and other minerals, typically stored in open storage fields, also referred to as stockpiles [104,105]. Another example is the transport of grain, corn, and starch, often done with pneumatic transport [106]. However, sodium borohydride and sodium metaborate are not among these conventional commodities, and there is no guarantee that existing handling and storage equipment is suitable for this new fuel and its respective spent fuels.

As discussed in the previous section, $NaBH_4$ is highly hygroscopic and, under most conditions, deliquescent; hence, closed storage is required. Furthermore, as temperature fluctuations during the day may lead to significant temperature ranges and moisture condensation inside the storage facility [107], climate control might be required. Next, the storage equipment should be designed to contain large quantities of fuel and spent fuel and be able to maintain and discharge the materials even after days or weeks of static storage. For such conditions, time consolidation (consolidation of a bulk material due to storage for an extended amount of time) could be an issue. $NaBH_4$ is an inorganic salt, and such materials are found to be affected by time consolidation by Stoklosa et al. [108], resulting in a reduced ability for the materials to flow (flowability). This means that the effects of time consolidation should be investigated and mitigated to ensure that the material's flowability—and therefore the ability to (dis)charge the materials from their storage systems—is maintained. Neglecting this could lead to malfunctioning and thus significant downtime and additional costs.

Aside from being stored, the sodium borohydride and sodium metaborate need to be transported across the port, and for transport of bulk solids, numerous types of equipment are available. An often-used solution is the belt conveyor, which can be used to transport bulk solids for over 98 km [109]. However, as with storage, an enclosed (controlled) environment is preferred, so the belt conveyor needs to be fully enclosed. Alternatively, conveying solutions such as a pipe conveyor, screw conveyor, or pneumatic conveyor might prove applicable as well. Moreover, the proposed circular bunkering process of Fig. 4 consists of various fuel and spent fuel flows. It can be expected that some of these flows have to be transferred between equipment, and for these tasks, e.g., transfer chutes can be used [110].

In addition, there are a number of logistical challenges: redistribution of the fuel and spent fuel due to differences between ports using trucks, trains, or even ships (that carry the (spent) fuel as cargo); transportation of the spent fuel to the regeneration facility; and the distribution of the fuel back to the ports, and also, placement of the regeneration facilities, but these challenges are out of scope and will therefore not be included in this work.

5. Vessel infrastructure

While the stored and transported fuel and spent fuel at the port side are always dry, solid flows, the expected material flows in the vessel are both liquid and solid. To illustrate this, Fig. 8 is constructed, where five material flows are shown. Note that the contents of this figure are already discussed alongside Fig. 3, but here more detail is given to the material flows.

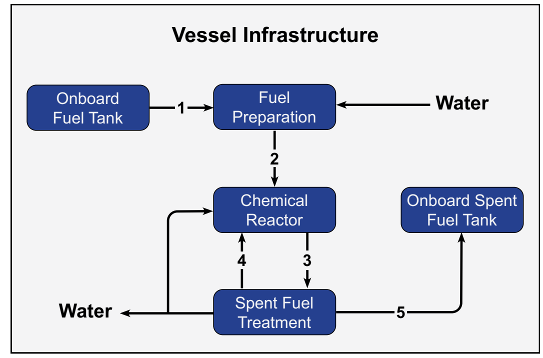

Fig. 8. Vessel infrastructure and process flows. (1) Solid flow of $NaBH_4$ to the fuel preparation. (2) Liquid flow of $NaBH_4$ solution to the reactor. (3) Liquid flow of a mixture of water, $NaBO_2{\cdot}xH_2O$, and unreacted $NaBH_4$. (4) Liquid flow of unreacted $NaBH_4$ solution. (5) Solid flow of $NaBO_2{\cdot}xH_2O$ to the spent fuel tank.

Actually, only two of the flows contain dry, solid material: flow 1 ($NaBH_4$) and flow 5 ($NaBO_2{\cdot}xH_2O$). The other flows are liquid, and as a result, a combination of (conventional) piping and pumping installations working alongside bulk handling and storage equipment is required inside the vessels. Next to this, the capacities of the required fuel tanks change, and there needs to be storage for the spent fuel onboard the ship. Furthermore, the fuel preparation, the reactor, and the spent fuel treatment also need to be placed inside the vessel, so first the capacity requirements for the vessel will be discussed.

5.1. Capacity requirements

Van Rheenen et al. [111] investigated the equipment sizing for the application of sodium borohydride as a maritime fuel. Their study involved a medium-sized vessel, such as a ferry or a small cargo ship, with a total power of 2 MW. They concluded that the chemical reactor and the spent fuel treatment equipment are important to include in ship design due to their considerable size, while the equipment required for mixing $NaBH_4$ with water is negligibly small. However, they did not take into account the sizing of the fuel and spent fuel tanks. To address this, we use Ammar et al. [112] to estimate the required storage tanks for sodium borohydride and the spent fuel. They analysed a 15,000 TEU container vessel, which has storage tanks of approximately 11,400 m^3 and a maximum continuous rating of 37.6 MW. Their analysis used diesel fuel with a lower heating value of 42.5 MJ/kg and a density of 850 kg/m^3, values that are also employed in this analysis. Similar to the port side analysis, Eqs. (4) and (6) can be used to translate the conventional fuel needs to the sodium borohydride and spent fuel requirements for the vessel infrastructure, and the results are shown in Fig. 9. Given the uncertainty regarding which form of spent fuel will be used on maritime vessels, the results for both hydrated ($NaBO_2{\cdot}2H_2O$ and $NaBO_2{\cdot}4H_2O$) and anhydrous ($NaBO_2$) sodium metaborate are provided. Also, the approach of Rheenen et al. is used to estimate the required size for the reactor and spent fuel treatment, and the mass is estimated by assuming thin-walled cylinders for both the reactor and the spent fuel treatment. It can be noted that although the size and mass of this equipment are not negligible, it is orders of magnitude smaller than the required storage capacity. The required storage capacity in terms of both mass and volume is affected by the transition from conventional diesel to sodium borohydride. The mass of required sodium borohydride is 60 % more than the required amount of fossil fuels, but even more noteworthy is the increasing mass of the vessel when converting $NaBH_4$ to spent fuel. Compared

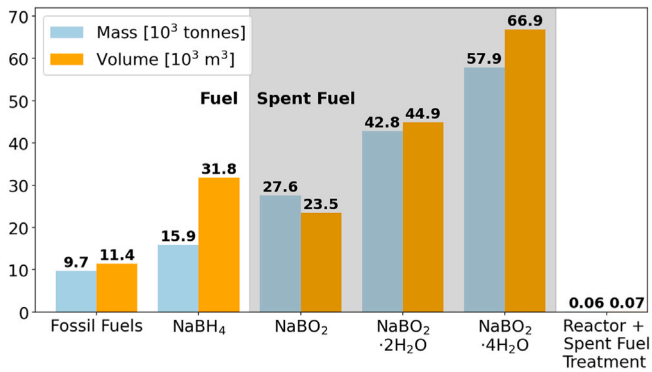

Fig. 9. Storage capacity for a 15,000 TEU container vessel. *The bulk densities of spent fuels are assumed to be 50 % of their particle densities, in line with documented bulk densities of sodium borohydride. **The expected size of the chemical reactor and spent fuel treatment is based on the results of van Rheenen et al. [111]. ***For the mass of the chemical reactor and spent fuel treatment, thin-walled cylinder tanks are assumed.

to the total mass of the $NaBH_4$, the spent fuel is 70 %, 170 %, and 260 % heavier, corresponding to anhydrous, dihydrate ($NaBO_2{\cdot}2H_2O$), and tetrahydrate ($NaBO_2{\cdot}4H_2O$) sodium metaborate. On the other hand, the anhydrous spent fuel reduces in volume by 30 %, while for the dihydrate and tetrahydrate, an increase of 40 % and 110 % can be seen, respectively.

5.2. Bunkering requirements

The bunkering requirements for the vessel's infrastructure will be discussed using Fig. 8. As flows 2, 3, and 4 are liquid flows, we assume conventional piping and pumping systems can be used. Flows 1 and 5 need to be able to handle a solid flow of sodium borohydride and sodium metaborate, respectively. Similar to the ports' infrastructure, the materials should not be exposed to ambient conditions, and consequently, handling equipment for these flows needs to be enclosed. Conversely, as the transport distances are relatively short, such that the material has no time to take up moisture from the ambient air, climate control may not be necessary.

The solid, granular $NaBH_4$ (flow 1) is extracted from the $NaBH_4$ storage tank, while flow 5 is discharged into the spent fuel tank. This could be (dual) fuel tanks or separate tanks. The benefit of a dual fuel tank is that less space is required during vessel operation. The tank capacity for sodium borohydride decreases, while at the same time, there is an increasing amount of spent fuel. Separation of the materials would require a flexible storage volume, for instance, by means of a moving wall inside the tank. This storage method has already been proposed by Lensing [64], but the feasibility of such a dual fuel tank solution depends on the material's mechanical characteristics, which have not yet been investigated thoroughly.

On the other hand, single storage tanks would take up more space. Although the exact spent fuel is not yet determined, the capacity requirements presented for a 15,000 TEU vessel (Fig. 9) can be used to estimate the effect of the additional storage space. Compared to dual fuel storage, the additional storage space would be at least 23,500 m^3. Assuming the volume of a twenty-foot container (1 TEU) is equal to 33.3 m^3 (6.06 m × 2.44 m × 2.59 m), an equivalent amount of 613 containers, or 4 % of the ship's capacity, has to be sacrificed to be able to carry the fuel and spent fuel. Regardless of the exact design of the storage tank(s), the effect of time consolidation should be investigated and, if needed, accounted for in the design of the equipment.

Another important requirement for the bunkering equipment inside the vessel is the ability to control the amount of fuel extracted from the fuel tank, i.e., being able to control the throughput of flow 1. This

Table 4
Air temperature distribution of the world's oceans [119].

	Temperature [°C]		
	Mean	Minimum	Maximum
Arctic Ocean	1.2	−1.9	10
North Atlantic Ocean	23	1.0	31
South Atlantic Ocean	22	12	31
North Pacific Ocean	19	1.0	30
South Pacific Ocean	25	15	31
Indian Ocean	26	19	32
Southern Ocean	2.1	−1.9	9.8

ensures that only the desired amount of $NaBH_4$ enters the fuel preparation. This is important since the mixture of fuel and water from the fuel preparation is fed to the chemical reactor, where hydrogen for the ships' fuel cells is produced. The amount of fuel in the reactor needs to be controlled to be able to have a variable power generation (without significant hydrogen buildup); hence, controlling the flow of $NaBH_4$ from the storage to the fuel preparation (flow 1) is essential.

5.3. Operational conditions

Unlike ports, which are fixed at a geographical location, ships move between ports across oceans, and therefore, the operational conditions experienced along the route are never constant. It is therefore evident that the bunkering equipment on ships has to be designed to account for this ever-changing environment. Still, an estimate of the operational conditions on the vessel can be made by looking at the average conditions on the world's seas. Shakespeare and Roderick [113] investigated the relative humidity at surface level of the world's oceans and concluded that, independent of time and geographical location, an average of 80 % RH can be experienced. They also showed that the air temperature a few meters above the sea surface is approximately the same as the sea surface water temperature (±4 degrees). Temperature is dependent on geographical location, and Table 4 presents the average temperature ranges for the air above different oceans. It is clear that the temperature varies significantly from ocean to ocean but also across the oceans. Therefore, when designing vessels using sodium borohydride as a fuel, the operational conditions presented in Tables 3 and 4 should be taken into account, together with the expected missions of the vessel, such that bunkering equipment can be designed accordingly.

Next to temperature and relative humidity, vibrations of the bunkering equipment should be considered. These vibrations are caused, e.g., by the impact of waves on the hull of the ship or by the ship's engines, and propagate through the vessel to reach the storage tanks and other bunkering equipment [114,115]. This can affect the characteristics and flowability of the materials during storage and handling [116–118], and consequently these vibrations should be taken into account in the design stage.

6. Bunkering equipment

This section presents examples of bunkering systems that fulfil the requirements described in the previous sections (e.g., closed system design). As most of the examples include both storage equipment and handling equipment, the term 'bunkering equipment' will be used to refer to the complete system. Furthermore, we discuss which material characteristics of $NaBH_4$ and the spent fuel(s) are required to enable effective equipment design. The aim of this section is to emphasise the importance of understanding the mechanical characteristics of $NaBH_4$ and its spent fuel(s) to support informed decisions in designing effective bunkering equipment and processes, rather than prescribing specific solutions.

The aim of this section is not to propose novel types of bunkering equipment nor to make a definitive selection of what should be used for this new fuel and its spent fuels. Rather, it is to highlight the importance

Fig. 10. Hopper storage with screw discharge and inclined transport [120].

of understanding the specific characteristics of $NaBH_4$ and the spent fuel(s) before substantiated decisions can be made regarding equipment and process design.

6.1. Hopper silo storage

Bunkering equipment for a novel circular fuel such as sodium borohydride should be enclosed, and a commonly used solution for this type of bunkering is a hopper silo fitted with a screw conveyor for discharge, of which an example can be seen in Fig. 10. A hopper silo is essentially a rectangular or circular bin, fitted with a hopper at the bottom. This hopper has a conical or wedge-like shape, and the bottom opening, or aperture, is connected to other equipment to facilitate the discharge of the materials from the silo. The main principle for silos and hoppers is determining the expected stresses on the equipment walls, so that it can be designed accordingly. To determine the horizontal stress exerted on the equipment walls in vertical sections, Eq. (7) can be used [95].

$$\sigma_h(z) = \frac{g\rho_b A}{\tan(\phi_x)U} + \left[1 - \exp\left(\frac{-K\tan(\phi_x)Uz}{A}\right)\right] \tag{7}$$

where σ_h denotes the horizontal stress on the silo walls, which is a function of the depth at which the stress is determined, z. Naturally, z is bounded between 0 and the total height of the silo, but an important note is that $z = 0$ at the free surface of the stored material, at the top of the silo. Also, σ_h depends on both equipment and material characteristics. Of the equipment, the circumference U and the area A (constant for the height of the silo) are required. The required material characteristics, also referred to as mechanical characteristics, are the bulk density ρ_b, the lateral stress ratio K (the ratio between the horizontal and vertical stress), the wall friction ϕ_x (friction between the bulk material and the equipment wall), and g, the gravitational acceleration. Often such silos are designed for a first-in-first-out principle, also known as mass flow. This means that while discharging, all material is in motion, and no material is left behind in the silo.

Additionally, the outlet dimensions at the bottom of the hopper need to be determined to ensure the stored material can discharge properly, and this can be calculated using Eq. (8) [95].

$$d_{c/p,crit} = H(\Theta_{c/p})\frac{\sigma_{c,crit}}{g\rho_{b,crit}} \tag{8}$$

where $d_{c/p,crit}$ is the critical outlet dimension for a conical (c) or a wedge-shaped hopper (p). $H(\Theta)$ is a function of the inclination of the conical (Θ_c) or wedge-shaped (Θ_p) hopper, and g denotes the gravitational acceleration. $\sigma_{c,crit}$ describes the stress required at the outlet opening to start discharge and is a function of the internal friction (friction between particles in the bulk material) and the geometry of the hopper. Lastly, $\rho_{b,crit}$ denotes the bulk density at the outlet conditions, which is a function of the stress exerted on the bulk material.

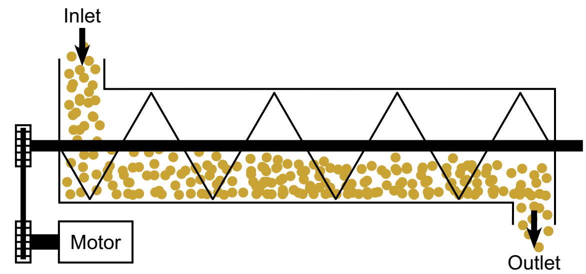

Fig. 11. Schematic view of a screw conveyor.

6.2. Screw conveyor

Often used equipment for discharge and transport of bulk materials is the screw conveyor, which has a fully enclosed design consisting of a circular or U-shaped tube in which a helix rotates (Fig. 11). The rotation of the helix causes the grains to be pushed along the bottom of the tube, and therefore a screw conveyor is rarely completely filled [121]. Because of the fully enclosed design, this solution is ideal for sodium borohydride, ensuring that the material cannot interact with the ambient air. Since the main objective of the screw conveyor is to discharge the silo and further transport the granular material, a good starting point for the evaluation of its operating principles would be to determine the volumetric flow rate ($\dot{Q}_V$) and the gravimetric flow rate ($\dot{Q}_M$) (Eqs. 9 and 10) [122,123].

$$\dot{Q}_V = \alpha\frac{\pi}{4}\left((D_{sc} + 2c)^2 - D_{sh}^2\right)(p - t)n \tag{9}$$

$$\dot{Q}_M = \dot{Q}_V \cdot \rho_b \tag{10}$$

where α is the filling rate, D_{sc} is the screw diameter, D_{sh} is the shaft diameter, c is the clearance between the tube/casing and the screw, p is the screw pitch, t is the thickness of the helix, n is the rotational speed of the helix, and ρ_b is the bulk density. At first glance, the volumetric flow rate $\dot{Q}_V$ does not depend on any material characteristics, but Waje et al. [122] state that the filling rate strongly depends on the mechanical characteristics of the conveyed bulk material. Furthermore, the motor power required to achieve the desired flow rate depends on additional information, such as the friction between the bulk material and the casing [121].

In addition, sodium borohydride is deliquescent when the relative humidity exceeds 19 %, and therefore conditioning the air inside the enclosed equipment is desirable. This can be achieved using a system based on the concept presented by Waje et al. [122], who designed a screw conveyor that actively dries the conveyed materials. Although they used it to dry wet materials, it can also be used to keep materials dry by supplying dry air or an inert gas, such as nitrogen, instead of a heated medium.

6.3. Tube chain conveyor

A different approach for a closed handling system for bulk materials is the tube chain conveyor [124–127]. Its main principle is based on the “damming up disc” principle. Transportation discs are fixed on a chain, which is pulled through a circular tube. The bulk material is therefore dragged along, and by filling the tube at one end while emptying it at the other, the bulk material is transported whilst protected from the outside environment. A picture of a real-life tube chain conveyor is shown in Fig. 12a, and a schematic illustration of the complete system can be seen in Fig. 12b. As the chain with filled pockets (a pocket is the gap

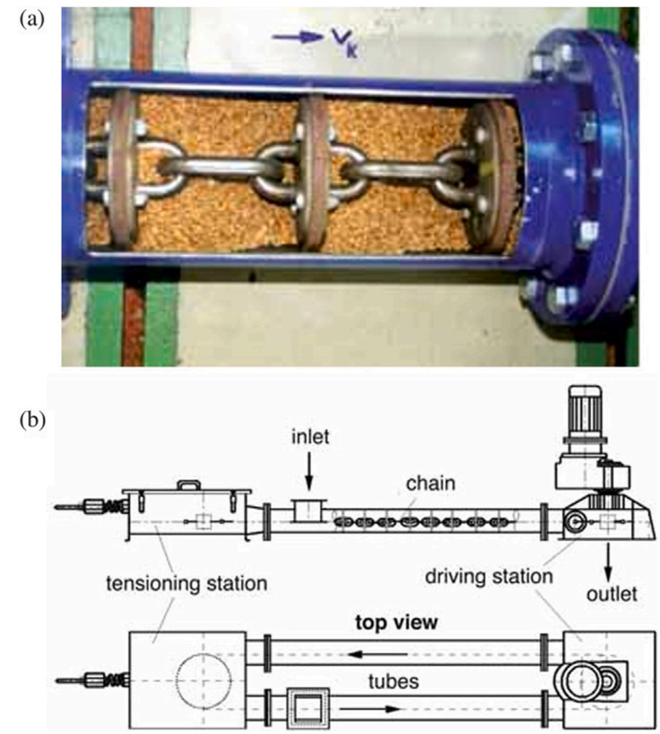

Fig. 12. Chain tube conveyor; (a) transportation of wheat; (b) schematic view of a horizontal tube chain conveyor. (Adapted from [124,126].)

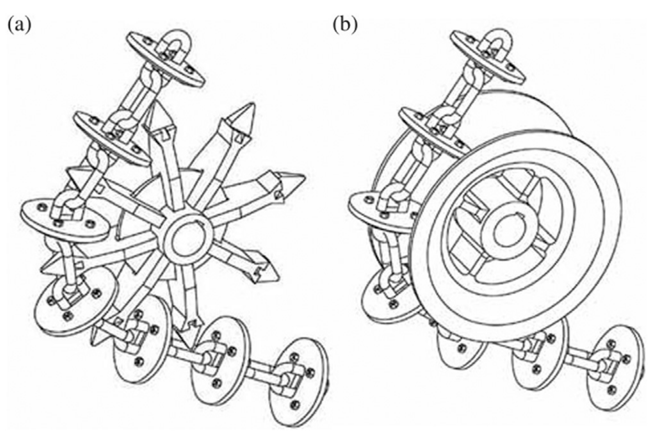

Fig. 13. Sprocket (a) and rim wheel (b) for redirection of a tube chain conveyor [126].

between two discs) is pulled through the tube from inlet to outlet, it also has to return to the inlet with empty pockets to pick up new bulk material. Therefore, it can be considered slightly more complex than a screw conveyor, where the helix simply rotates at a fixed position inside the tube. However, unlike most mechanical conveyors, its main benefit is that the chain tube conveyor can be used to transport bulk material in all three dimensions [125]. But, instead of simply pulling the chain through a multi-directional tube, using either a sprocket or rim wheel to redirect its direction can improve its efficiency, and these two mechanisms are shown in Fig. 13. The mass flow ($\dot{Q}_M$) of such a system can be expressed with Eq. (11), adapted from [124].

$$\dot{Q}_M = \eta \frac{\pi D_{R_i}^2}{4} \rho_b V \tag{11}$$

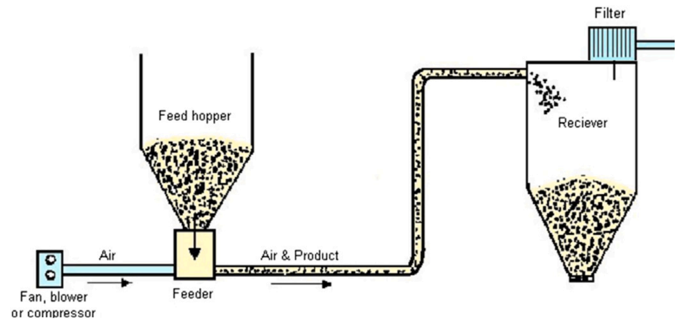

Fig. 14. Schematics of pneumatic conveying [134].

where η accounts for the filling and transport efficiency, which depends mainly on the geometry (e.g., volume of the tube compared to the transportation discs and chain), D_{R_i} denotes the radius of the tube, ρ_b is the bulk density, and V is the chain speed. Next to the mass flow, the drag force that is required to pull the chain through the tube also depends on some material characteristics, such as the lateral stress ratio K and the friction between the particles.

Other transport equipment options are the (enclosed) belt conveyor [128], the pipe belt conveyor [129–131], and the (enclosed) chain conveyor [132,133]. As the working principles of the chain conveyor are similar to the tube chain conveyor, this will not be elaborated on here. Furthermore, since exposure of sodium borohydride to ambient air has to be minimised, we think the (enclosed) belt conveyor and the pipe belt conveyor are less feasible for this purpose, but they are not excluded from consideration yet.

6.4. Pneumatic conveying

Instead of mechanical conveying by means of a screw or tube chain conveyor, where the bulk material is either pushed or dragged by a mechanical device, pneumatic conveying uses a gas, mostly air, to transport bulk materials. A schematic view of a pneumatic conveying system is presented in Fig. 14. Its main features are a feed hopper, either a fan, blower, or compressor, a conveying pipeline, and a receiver hopper. The main benefit of pneumatic conveying is that the only moving media are the bulk material and the gas that conveys the materials, and this can be normal air, dry air, or any other gas that is desired. Note that the humidity of the conveying gas has to be sufficiently dry when transporting $NaBH_4$, due to its hygroscopic nature. Furthermore, the bulk material can be conveyed in three dimensions for long distances, as long as there is sufficient pressure drop. The hopper must be designed according to Eq. (7). The pressure drop ΔP depends on both geometrical aspects and the mechanical characteristics of the conveyed material [134] and can be determined using Eq. (12) [135]. The pressure drop can in turn be used to calculate the mass flow ($\dot{Q}_M$) using Eqs. (13) and (14).

$$\Delta P = \frac{2 f_m V_s^2 \rho_b L}{D} \tag{12}$$

$$\dot{Q}_M = \rho_b V_s D^2/4 \tag{13}$$

$$\dot{Q}_M = \frac{\Delta P}{8 f_m V_s} \frac{D^3}{L} \tag{14}$$

where L and D are the length and diameter of the pipe, respectively, f_m is the friction factor, rho_b is the bulk density, and V_s is the particle velocity. Please note that this equation is valid for straight sections and is merely used here to illustrate the importance of the mechanical characteristics of the materials that have to be conveyed. When introducing bends, as often present in real-life applications, common practice is to gather experimental data to determine the pneumatic conveying characteristics in order to design a system properly [134].

In the presented pneumatic conveying system, the bulk material is fed to the pipeline by means of a rotary valve, but this can also be done using a screw conveyor. Furthermore, instead of discharging at the bottom of the hopper, the system can also be designed such that the bulk material in the hopper is fluidised and exits at the top of the storage tank, and these systems are often referred to as blowtanks [134,136,137]. Regardless of the exact configuration of the pneumatic conveying system, the main working principles remain unchanged, and still (many) mechanical characteristics of the to-be-conveyed materials are required.

Concluding, although seemingly simple at first sight, a thorough understanding of the mechanical characteristics of a bulk material is needed before a substantiated choice for the bunkering equipment can be made, a conclusion that is supported by the work of Waje et al. [122]. Consequently, to design the circular bunkering infrastructure as presented in Figs. 3 and 4, the mechanical characteristics of both sodium borohydride and sodium metaborate are required.

7. Mechanical characteristics

A granular material has many different mechanical characteristics, and they can be categorised into three main groups: particle characteristics, bulk characteristics, and interface characteristics [101]. Particle characteristics describe individual properties such as density, size, shape, roughness, and hardness. Bulk characteristics encompass the behaviour of a collection of particles, including interactions like bulk density, angle of repose, inter-particle friction, cohesion, and particle size distributions. Interface characteristics involve interactions between the bulk material and equipment, including wall friction, adhesion, and the ratio between particle size and characteristic size of the equipment [138–143].

It is important to note that these mechanical characteristics are not static but can vary significantly with operational conditions such as humidity, stress, and temperature. For example, increased moisture content can lead to the formation of liquid bridges between particles, increasing cohesion and consequently reducing flowability [88,144]. Operational stresses, such as handling or time-dependent consolidation, can result in particle attrition, breakage [145], or deformation of the particle bed. These effects alter particle size and shape distributions, which, through mechanisms such as van der Waals forces, influence flowability by affecting properties like cohesion, angle of repose, wall friction, and internal friction [108,146–149]. Temperature fluctuations also impact flowability [150], induce sintering [151], cause thermal expansion of individual particles [89], and affect bulk density by altering the material's moisture content. To summarise, an overview of the various mechanical characteristics and influential operational conditions is illustrated in Fig. 15.

While the effects of operational conditions on mechanical characteristics are well-documented in general—such as increased cohesion due to liquid bridge formations—no experimental data are currently available that specifically examine how these conditions affect sodium borohydride and its spent fuels. However, some general mechanical characteristics have been reported, albeit minimally. Nagar et al. [35] describe the modelling of $NaBH_4$ and report some particle-particle characteristics: the internal friction, cohesion, and the angle of repose, and they also describe the particle size. Ghellab et al. [152] investigate the elastic, mechanical, and thermodynamic properties of $NaBH_4$ on the molecular scale. While we focus on the micro (particle) to macro (bulk) scale, their analysis provides valuable insights into characteristics such as the shear modulus and the Poisson's ratio of $NaBH_4$ particles. The authors of [153] discuss the angle of repose of the spent fuel, but it was not specified which sodium metaborate (anhydrous, dihydrate, or tetrahydrate) was used. Lastly, Muradov [154] reports that for storage of $NaBH_4$ slurries, the wall material of the storage tank should be considered carefully. They find that copper, carbon steel, and brass act as catalysts for the hydrolysis reaction, while glass, polyethylene, and stainless steel are suitable. Although we do not consider slurries in this work, the deliquescent nature of $NaBH_4$ suggests that such behaviour could occur under high humidity, making these findings relevant.

To the best of the author's knowledge, these are the only mechanical characteristics of $NaBH_4$ and its spent fuels that are described in literature, highlighting the need for further research into this novel fuel and its spent fuels.

8. Conclusion

This paper demonstrated that transitioning to solid hydrogen carriers as alternative fuels requires significant adaptations to the bunkering systems of both ports and vessels. Given their granular nature, their sensitivity to time consolidation, and their low humidity storage requirements, the bunkering equipment on both the vessels and at the ports must be redesigned. If these requirements are not properly implemented, issues with flowability could arise, potentially leading to power

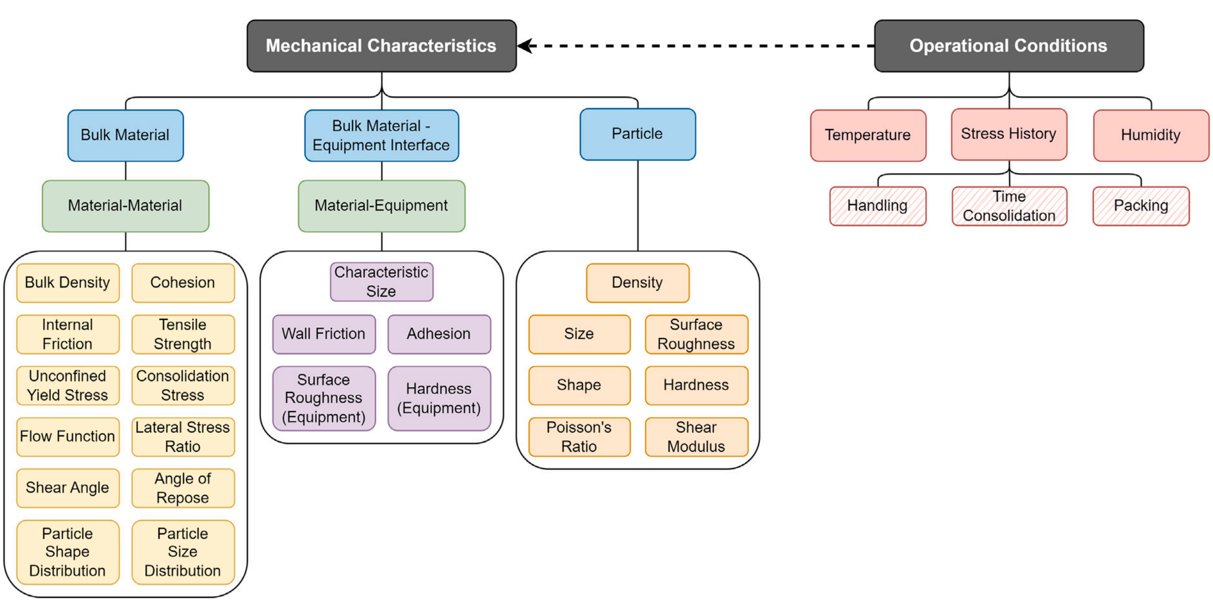

Fig. 15. Overview of different material characteristics and influential operational conditions. (Adapted from [101].)

loss on vessels and logistical challenges at ports. Second, the port infrastructure must accommodate handling and storing the spent fuel that is returned from the vessels. This expansion includes additional handling equipment to transport the metaborate from the vessels to the storage facilities. Furthermore, an increase in storage capacity in both ports and vessels might be required due to the lower energy density of sodium borohydride compared to conventional fuels. Lastly, the vessel infrastructure also requires adjustments. Instead of a liquid fuel tank and a diesel engine, vessels will need dual (granular) fuel storage tanks and a chemical reactor.

9. Recommendations

This research contributed to shaping the roadmap towards alternative fuels in maritime shipping by exploring the potential of $NaBH_4$ as a hydrogen carrier. While the deliquescence limits of $NaBH_4$ have been investigated already, further research is necessary to validate these conclusions under (controlled) realistic and variable port environments. In particular, the flow behaviour and mechanical characteristics of both $NaBH_4$ and its spent fuels should be investigated in the context of storage, handling, and also the regeneration processes. This includes characterising their mechanical and flow properties and the effect of operational conditions, such as temperature, humidity fluctuations, and mechanical stresses, to ensure reliable performance.

Moreover, the regeneration of spent fuel remains a critical challenge, and more research is required to evaluate the energy requirements, reaction kinetics, and integration potential of regeneration systems within port infrastructure. At the same time, the logistical feasibility of circular bunkering systems should be assessed, including the identification of ports that can support such operations and the associated storage and transport requirements. These insights, along with the proposed port and vessel adaptations, can inform future decision-making frameworks for port and vessel transitions.

To support such decision-making, it is recommended that future studies build on these findings to develop comparative frameworks for evaluating hydrogen carrier technologies. These frameworks could help stakeholders assess trade-offs between technical feasibility, infrastructure compatibility, and environmental impact.

A key limitation of this study is the limited availability of empirical data on the mechanical characteristics and flow behaviour of solid-state $NaBH_4$. Although it is assumed to be free-flowing under controlled conditions, this has not been conclusively demonstrated in scientific literature. Furthermore, while the effects of temperature and humidity on laboratory-scale samples of $NaBH_4$ have been reported, little is known about the behaviour of bulk quantities under similar conditions.

While the question of scaling up the proposed technologies is important, it may be premature to address it in detail. Many of the required systems for bunkering—such as closed storage, dry conveying, and climate control—already exist in other industrial applications. Therefore, the immediate focus should be on investigating the mechanical characteristics of $NaBH_4$ and its spent fuels to determine whether existing systems can be adapted for this purpose or whether new, dedicated solutions must be developed.

CRediT authorship contribution statement

M.C. van Benten: Conceptualization, Methodology, Data Curation, Visualisation, Writing – Original draft preparation. **J.T. Padding:** Writing – Review & Editing, Supervision, Funding acquisition. **D.L. Schott:** Writing – Review & Editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is part of the project SH2IPDRIVE with project number MOB21013, funded by the Ministry of Economic Affairs and Climate Policy, RDM regulation, carried out by the Netherlands Enterprise Agency.

Data availability

Data will be made available upon request.

References

[1] Cassia R, Nocioni M, Correa-Aragunde N, Lamattina L. Climate change and the impact of greenhouse gasses: CO_2 and NO, friends and foes of plant oxidative stress. Front Plant Sci 2018 Mar; 9. ISSN 1664-462X. https://doi.org/10.3389/fpls.2018.00273

[2] Segger MC. Advancing the paris agreement on climate change for sustainable development. Camb Int Law J 2016 Jun. https://doi.org/10.4337/cilj.2016.02.03

[3] Liu H, Mao Z, Li X. Analysis of international shipping emissions reduction policy and China's participation. Front Mar Sci 2023 Jan;10. ISSN 2296-7745. https://doi.org/10.3389/fmars.2023.1093533

[4] IMO. UN body adopts climate change strategy for shipping. https://www.imo.org/en/MediaCentre/PressBriefings/Pages/06GHGinitialstrategy.aspx; 2018 Apr.

[5] Yuan Y, Wang J, Yan X, Shen B, Long T. A review of multi-energy hybrid power system for ships. Renew Sustain Energy Rev 2020 Oct;132:110081. ISSN 1364-0321. https://doi.org/10.1016/j.rser.2020.110081

[6] Inal OB, Charpentier JF, Deniz C. Hybrid power and propulsion systems for ships: current status and future challenges. Renew Sustain Energy Rev 2022 Mar;156:111965. ISSN 1364-0321. https://doi.org/10.1016/j.rser.2021.111965

[7] Rivard E, Trudeau M, Zaghib K. Hydrogen storage for mobility: a review. Materials 2019 Jun;12(12):1973. ISSN 1996-1944. https://doi.org/10.3390/ma12121973

[8] Usman MR. Hydrogen storage methods: review and current status. Renew Sustain Energy Rev 2022 Oct;167:112743. ISSN 1364-0321. https://doi.org/10.1016/j.rser.2022.112743

[9] van Rheenen ES, Padding JT, Slootweg C, Visser K. A review of the potential of hydrogen carriers for zero emission, low signature ship propulsion systems. In: Conference proceedings of INEC; 2022. https://doi.org/10.24868/10649

[10] Brunel JM. Polysilanes: the grail for a highly-neglected hydrogen storage source. Int J Hydrogen Energy 2017 Sep;42(36):23004–09. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2017.07.206

[11] McKinlay CJ, Turnock S, Hudson D. A comparison of hydrogen and ammonia for future long distance shipping fuels. In: LNG/LPG and alternative fuel ships (29/01/20–30/01/20); 2020 Jan. p. 53–65.

[12] Makepeace JW, He T, Weidenthaler C, Jensen TR, Chang F, Vegge T, et al. Reversible ammonia-based and liquid organic hydrogen carriers for high-density hydrogen storage: recent progress. Int J Hydrogen Energy 2019 Mar;44(15):7746–67. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2019.01.144

[13] Niermann M, Beckendorff A, Kaltschmitt M, Bonhoff K. Liquid organic hydrogen carrier (LOHC) – assessment based on chemical and economic properties. Int J Hydrogen Energy 2019 Mar;44(13):6631–54. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2019.01.199

[14] Shet SP, Shanmuga P. S, Sudhakar K, Tahir M. A review on current trends in potential use of metal-organic framework for hydrogen storage. Int J Hydrogen Energy 2021 Mar;46(21):11782–803. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2021.01.020

[15] Moradi R, Groth KM. Hydrogen storage and delivery: review of the state of the art technologies and risk and reliability analysis. Int J Hydrogen Energy 2019 May;44(23):12254–69. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2019.03.041

[16] Habibi P, Postma JRT, Padding JT, Dey P, Vlugt TJH, Moultos OA. Thermodynamic and transport properties of $H2/H_2O/NaB(OH)4$ mixtures using the Delft force Field (DFF/B(OH)4–). Ind Eng Chem Res 2023 Aug;62(30):11992–2005. ISSN 0888-5885. https://doi.org/10.1021/acs.iecr.3c01422

[17] Langmi HW, Engelbrecht N, Modisha PM, Bessarabov D. Chapter 13 - Hydrogen storage. In Smolinka T, Garche J, editors. Electrochemical power sources: fundamentals, systems, and applications. Elsevier; 2022 Jan. p. 455–86. ISBN 978-0-12-819424-9. https://doi.org/10.1016/B978-0-12-819424-9.00006-9

[18] Jaiswal A, Sahoo RK, Ray SS, Sahu S. Alkali metals decorated silicon clusters ($SinMn$, $n = 6, 10$; $M = Li, Na$) as potential hydrogen storage materials: a DFT study. Int J Hydrogen Energy 2022 Jan;47(3):1775–89. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2021.10.228

[19] Kojima Y. Hydrogen storage materials for hydrogen and energy carriers. Int J Hydrogen Energy 2019 Jul;44(33):18179–92. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2019.05.119

[20] Wang L, Quadir MZ, Aguey-Zinsou KF. Direct and reversible hydrogen storage of lithium hydride (LiH) nanoconfined in high surface area graphite. Int J Hydrogen Energy 2016 Oct;41(40):18088–94. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2016.07.073

[21] van Hoecke L, Laffineur L, Campe R, Perreault P, Verbruggen SW, Lenaerts S. Challenges in the use of hydrogen for maritime applications. Energy Environ Sci 2021 Feb;14(2):815–43. ISSN 1754-5706. https://doi.org/10.1039/D0EE01545H

[22] Salman MS, Lai Q, Luo X, Pratthana C, Rambhujun N, Costalin M, et al. The power of multifunctional metal hydrides: a key enabler beyond hydrogen storage.

J Alloys Compd 2022 Nov;920:165936. ISSN 0925-8388. https://doi.org/10.1016/j.jallcom.2022.165936
[23] Demirci UB. Ammonia Borane: an extensively studied, though not yet implemented, hydrogen carrier. Energies 2020 Jan;13(12):3071. ISSN 1996-1073. https://doi.org/10.3390/en13123071
[24] Wu H, Cheng Y, Fan Y, Lu X, Li L, Liu B, et al. Metal-catalyzed hydrolysis of ammonia borane: mechanism, catalysts, and challenges. Int J Hydrogen Energy 2020 Nov;45(55):30325–40. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2020.08.131
[25] Stephens FH, Pons V, Baker RT. Ammonia–borane: the hydrogen source par excellence? Dalton Trans 2007 Jun;2613–26. ISSN 1477-9234. https://doi.org/10.1039/B703053C
[26] Lang C, Jia Y, Yao X. Recent advances in liquid-phase chemical hydrogen storage. Energy Storage Mater 2020 Apr;26:290–312. ISSN 2405-8297. https://doi.org/10.1016/j.ensm.2020.01.010
[27] Shimbayashi T, Fujita K-I. Metal-catalyzed hydrogenation and dehydrogenation reactions for efficient hydrogen storage. Tetrahedron 2020 Mar;76(11):130946. ISSN 0040-4020. https://doi.org/10.1016/j.tet.2020.130946
[28] Giannis A, Sandhoff K. LiBH4($NaBH_4$)/Me3SiCl, an unusually strong and versatile reducing agent. Angew Chem Int Ed Engl 1989 Feb;28(2):218–20. ISSN 0570-0833, 1521-3773. https://doi.org/10.1002/anie.198902181
[29] Toda F, Kiyoshige K, Yagi M. $NaBH_4$ reduction of ketones in the solid state. Angew Chem Int Ed Engl 1989 Mar;28(3):320–21. ISSN 0570-0833, 1521-3773. https://doi.org/10.1002/anie.198903201
[30] Liu QM, Zhou D, Yamamoto Y, Ichino R, Okido M. Preparation of Cu nanoparticles with $NaBH_4$ by aqueous reduction method. Trans Nonferrous Met Soc China 2012 Jan;22(1):117–23. ISSN 10036326. https://doi.org/10.1016/S1003-6326(11)61149-7
[31] Zhang K, Suh JM, Choi JW, Jang HW, Shokouhimehr M, Varma RS. Recent advances in the Nanocatalyst-assisted $NaBH_4$ reduction of nitroaromatics in water. ACS Omega 2019 Jan;4(1):483–95. ISSN 2470-1343, 2470-1343. https://doi.org/10.1021/acsomega.8b03051
[32] Liao G, Gong Y, Zhong L, Fang J, Zhang L, Xu Z, et al. Unlocking the door to highly efficient Ag-based nanoparticles catalysts for $NaBH_4$-assisted nitrophenol reduction. Nano Research 2019 Oct;12(10):2407–36. ISSN 1998-0124, 1998-0000. https://doi.org/10.1007/s12274-019-2441-5
[33] Kantürk Figen A, Pişkin S. Microwave assisted green chemistry approach of sodium metaborate dihydrate ($NaBO_2 \cdot 2H_2O$) synthesis and use as raw material for sodium borohydride ($NaBH_4$) thermochemical production. Int J Hydrogen Energy 2013 Mar;38(9):3702–09. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2013.01.003
[34] Çakanyildirim Ç, Gürü M. The production of $NaBH_4$ from its elements by mechanochemical reaction and usage in hydrogen recycle. Energy Sources Part A Recovery Utilization Environ Eff 2011 Jul;33(20):1912–20. ISSN 1556-7036, 1556-7230. https://doi.org/10.1080/15567030903503175
[35] Nagar Y, Schechter A, Ben-Moshe B, Shvalb N. Modeling the mechanical behavior of sodium borohydride ($NaBH_4$) powder. Mater Des 2016 Oct;108:240–49. ISSN 02641275. https://doi.org/10.1016/j.matdes.2016.06.077
[36] Brack P, Dann SE, Wijayantha KGU. Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride ($NaBH_4$) solutions. Energy Sci Eng 2015 May;3(3):174–88. ISSN 20500505. https://doi.org/10.1002/ese3.67
[37] Chandra D, Reilly JJ, Chellappa R. Metal hydrides for vehicular applications: the state of the art. JOM 2006 Feb;58(2):26–32. ISSN 1047-4838, 1543-1851. https://doi.org/10.1007/s11837-006-0005-0
[38] Urgnani J, Torres FJ, Palumbo M, Baricco M. Hydrogen release from solid state $NaBH_4$. Int J Hydrogen Energy 2008 Jun;33(12):3111–15. ISSN 03603199. https://doi.org/10.1016/j.ijhydene.2008.03.031
[39] Christian ML, Aguey-Zinsou KF. Core–Shell strategy leading to high reversible hydrogen storage capacity for $NaBH_4$. ACS Nano 2012 Sep;6(9):7739–51. ISSN 1936-0851, 1936-086X. https://doi.org/10.1021/nn3030018
[40] Martelli P, Caputo R, Remhof A, Mauron P, Borgschulte A, Züttel A. Stability and decomposition of $NaBH_4$. J Phys Chem C 2010 Apr;114(15):7173–77. ISSN 1932-7447, 1932-7455. https://doi.org/10.1021/jp909341z
[41] Mao J, Guo Z, Yu X, Liu H. Improved hydrogen storage properties of $NaBH_4$ destabilized by CaH_2 and $Ca(BH_4)_2$. J Phys Chem C 2011 May;115(18):9283–90. ISSN 1932-7447, 1932-7455. https://doi.org/10.1021/jp2020319
[42] Kumar S, Jain A, Miyaoka H, Ichikawa T, Kojima Y. Study on the thermal decomposition of $NaBH_4$ catalyzed by ZrCl4. Int J Hydrogen Energy 2017 Aug;42(35):22432–37. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2017.02.060
[43] Umegaki T, Yan JM, Zhang XB, Shioyama H, Kuriyama N, Xu Q. Boron- and nitrogen-based chemical hydrogen storage materials. Int J Hydrogen Energy 2009 Mar;34(5):2303–11. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2009.01.002
[44] Shang Y, Chen R. Hydrogen storage via the hydrolysis of $NaBH_4$ basic solution: optimization of $NaBH_4$ concentration. Energy Fuels 2006 Sep;20(5):2142–48. ISSN 0887-0624, 1520-5029. https://doi.org/10.1021/ef050363q
[45] Lee J, Kong KY, Jung CR, Cho E, Yoon SP, Han J, et al. A structured Co–B catalyst for hydrogen extraction from $NaBH_4$ solution. Catal Today 2007 Feb;120(3–4):305–10. ISSN 09205861. https://doi.org/10.1016/j.cattod.2006.09.019
[46] Aiello R. Production of hydrogen from chemical hydrides via hydrolysis with steam. Int J Hydrogen Energy 1999 Dec;24(12):1123–30. ISSN 03603199. https://doi.org/10.1016/S0360-3199(99)00002-6
[47] Marrero-Alfonso EY, Gray JR, Davis TA, Matthews MA. Minimizing water utilization in hydrolysis of sodium borohydride: the role of sodium metaborate hydrates. Int J Hydrogen Energy 2007 Dec;32(18):4723–30. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2007.08.014
[48] Senoh H, Siroma Z, Fujiwara N, Yasuda K. A fundamental study on electrochemical hydrogen generation from borohydrides. J Power Sources 2008 Oct;185(1):1–5. ISSN 03787753. https://doi.org/10.1016/j.jpowsour.2008.07.029
[49] Marchionni A, Bevilacqua M, Filippi J, Folliero MG, Innocenti M, Lavacchi A, et al. High volume hydrogen production from the hydrolysis of sodium borohydride using a cobalt catalyst supported on a honeycomb matrix. J Power Sources 2015 Dec;299:391–97. ISSN 03787753. https://doi.org/10.1016/j.jpowsour.2015.09.006
[50] Xueping Z, Xiangsheng Y, Xinyue L, Runnan J, Yongsheng Z, Zhihao Z, et al. Hydrogen storage performance of HPSB hydrogen storage materials. Chem Phys Lett 2019 Nov;734:136697. ISSN 00092614. https://doi.org/10.1016/j.cplett.2019.136697
[51] Chen W, Ouyang LZ, Liu JW, Yao XD, Wang H, Liu ZW, et al. Hydrolysis and regeneration of sodium borohydride ($NaBH_4$) – a combination of hydrogen production and storage. J Power Sources 2017 Aug;359:400–07. ISSN 0378-7753. https://doi.org/10.1016/j.jpowsour.2017.05.075
[52] Jeong SU, Kim RK, Cho EA, Kim HJ, Nam SW, Oh I-H, et al. A study on hydrogen generation from $NaBH_4$ solution using the high-performance Co-B catalyst. J Power Sources 2005 Jun;144(1):129–34. ISSN 03787753. https://doi.org/10.1016/j.jpowsour.2004.12.046
[53] Gislon P, Monteleone G, Prosini P. Hydrogen production from solid sodium borohydride. Int J Hydrogen Energy 2009 Jan;34(2):929–37. ISSN 03603199. https://doi.org/10.1016/j.ijhydene.2008.09.105
[54] Alligier D, Petit E, Demirci UB. A boron-11 NMR study of the stability of the alkaline aqueous solution of sodium borohydride that is both an indirect fuel and a direct fuel for low-temperature fuel cells. Int J Hydrogen Energy 2022 Jun;47(55):23310–15. ISSN 03603199. https://doi.org/10.1016/j.ijhydene.2022.05.119
[55] Arzac GM, Fernández A, Justo A, Sarmiento B, Jiménez MA, Jiménez MM. Optimized hydrogen generation in a semicontinuous sodium borohydride hydrolysis reactor for a 60W-scale fuel cell stack. J Power Sources 2011 May;196(9):4388–95. ISSN 03787753. https://doi.org/10.1016/j.jpowsour.2010.10.073
[56] Luo N, Miley GH, Mather J, Burton R, Hawkins G, Byrd E, et al. A kW-class $NaBH_4/H_2O_2$ fuel cell for air Independent propulsion. In: ASME 2006 fourth international conference on fuel cell science, engineering and technology, Parts A and B, Irvine, California, USA; 2006 Jan; 333–38. ISBN 978-0-7918-4247-8, 978-0-7918-3780-1. https://doi.org/10.1115/FUELCELL2006-97207
[57] Ma J, Choudhury NA, Sahai Y. A comprehensive review of direct borohydride fuel cells. Renew Sustain Energy Rev 2010 Jan;14(1):183–99. ISSN 1364-0321. https://doi.org/10.1016/j.rser.2009.08.002
[58] Miley GH, Luo N, Mather J, Burton R, Hawkins G, Gu L, et al. Direct $NaBH_4/H_2O_2$ fuel cells. J Power Sources 2007 Mar;165(2):509–16. ISSN 03787753. https://doi.org/10.1016/j.jpowsour.2006.10.062
[59] Mohring RM, Luzader RE. A sodium borohydride on-board hydrogen generator for powering fuel cell and internal combustion engine vehicles. In: Future transportation technology conference & exposition; Aug 2001. p. 2001–01-2529. https://doi.org/10.4271/2001-01-2529
[60] Kim T. $NaBH_4$ (sodium borohydride) hydrogen generator with a volume-exchange fuel tank for small unmanned aerial vehicles powered by a PEM (proton exchange membrane) fuel cell. Energy 2014 May;69:721–27. ISSN 03605442. https://doi.org/10.1016/j.energy.2014.03.066
[61] Kwon S, Kim MJ, Kang S, Kim T. Development of a high-storage-density hydrogen generator using solid-state $NaBH_4$ as a hydrogen source for unmanned aerial vehicles. Appl Energy 2019 Oct;251:113331. ISSN 03062619. https://doi.org/10.1016/j.apenergy.2019.113331
[62] Santos DMF, Sequeira CAC. Sodium borohydride as a fuel for the future. Renew Sustain Energy Rev 2011 Oct;15(8):3980–4001. ISSN 1364-0321. https://doi.org/10.1016/j.rser.2011.07.018
[63] Rivarolo M, Improta O, Magistri L, Panizza M, Barbucci A. Thermo-economic analysis of a hydrogen production system by sodium borohydride ($NaBH_4$). Int J Hydrogen Energy 2018 Jan;43(3):1606–14. ISSN 0360-3199. https://doi.org/10.1016/j.ijhydene.2017.11.079
[64] Lensing D. A study on the integration of a novel $NaBH_4$ fuelled hybrid system for a small inland vessel [Master thesis]. 2020 Apr.
[65] Jha S. Indian navy looks forward to DRDO's air independent propulsion system for submarines; 2017 Oct. https://delhidefencereview.com/2017/10/07/indian-navy-looks-forward-to-drdos-air-independent-propulsion-system-for-submarines/
[66] Raghunandan D. Indian navy's indigenisation push gets boost with AIP system for submarines; 2021 Mar. https://www.newsclick.in/indian-navy-indigenisation-push-gets-boost-AIP-system-submarines.
[67] Nievelt FM. Maritime application of sodium borohydride asan energy carrier. 2019 Feb. TU Delft Repository. Retrieved from https://repository.tudelft.nl/
[68] Düll A, Rohlfs P, Deutschmann O, Börnhorst M. Performance evaluation of KBH_4 as energy carrier for shipping applications. Chem Ing Tech 2022 May;94(5):747–59. ISSN 0009-286X, 1522-2640. https://doi.org/10.1002/cite.202100193
[69] Port of Rotterdam, Bunkeren in Rotterdam. https://www.portofrotterdam.com/nl/zeevaart/bunkeren-in-rotterdam
[70] Port of Rotterdam, King 3.0. https://www.portofrotterdam.com/nl/zeevaart/boeien-en-palen/king-30
[71] Port of Amsterdam, Facilities. https://www.portofamsterdam.com/en/shipping/inland-shipping/facilities
[72] Port of Amsterdam, Titan. https://myport.portofamsterdam.com/en/portle/company/titan

[73] Pichegru L, Vibert L, Thiebault A, Charrier I, Stander N, Ludynia K, et al. Maritime traffic trends around the southern tip of Africa – did marine noise pollution contribute to the local penguins' collapse? Sci Total Environ 2022 Nov;849:157878. ISSN 00489697. https://doi.org/10.1016/j.scitotenv.2022.157878
[74] Roos DMD. A single-objective, multi-period optimization model of an alternative maritime fuel supply chain network in the Port of Amsterdam [Thesis]. 2020 Dec.
[75] van den Berg M. LNG as fuel for inland waterway vessels. 2015 Sep. TU Delft Repository. Retrieved from https://repository.tudelft.nl/
[76] Qi J, Wang S. LNG bunkering station deployment problem—A case study of a Chinese container shipping network. Mathematics 2023 Feb;11(4):813. ISSN 2227-7390. https://doi.org/10.3390/math11040813
[77] Guo Y, Yan R, Qi J, Liu Y, Wang S, Zhen L. LNG bunkering infrastructure planning at port. Multimodal Transp 2024 Jun;3(2):100134. ISSN 27725863. https://doi.org/10.1016/j.multra.2024.100134
[78] DNV. RH2INE Kickstart Study. 2021. https://rh2ine.eu/about/kickstart-study
[79] Schotman HV. Ammonia bunkering and storage for the maritime industry during a global ammonia transitions. 2023 May. TU Delft Repository. Retrieved from https://repository.tudelft.nl/
[80] Hofste PC, Van Veldhuizen BN, Duinkerken MB, Schott DL. Design of an ammonia bunker installation for sea-going vessels - a best worst method approach. 1 ed. London: CRC Press; 2024 May. p. 11–21. ISBN 978-1-003-50877-9. https://doi.org/10.1201/9781003508779-2
[81] Jeong B, Lee BS, Zhou P, Ha S. Determination of safety exclusion zone for LNG bunkering at fuel-supplying point. Ocean Eng 2018 Mar;152:113–29. ISSN 0029-8018. https://doi.org/10.1016/j.oceaneng.2018.01.066
[82] Zhu Y, Ouyang L, Zhong H, Liu J, Wang H, Shao H, et al. Closing the loop for hydrogen storage: facile regeneration of $NaBH_4$ from its hydrolytic product. Angew Chem 2020 May;132(22):8701–07. ISSN 0044-8249, 1521-3757. https://doi.org/10.1002/ange.201915988
[83] Laversenne L, Goutaudier C, Chiriac R, Sigala C, Bonnetot B. Hydrogen storage in borohydrides comparison of hydrolysis conditions of LiBH4, $NaBH_4$ and KBH4. J Therm Anal Calorim 2008 Dec;94(3):785–90. ISSN 1572-8943. https://doi.org/10.1007/s10973-008-9073-4
[84] Ouyang L, Chen W, Liu J, Felderhoff M, Wang H, Zhu M. Enhancing the regeneration process of consumed $NaBH_4$ for hydrogen storage. Adv Energy Mater 2017 Oct;7(19):1700299. ISSN 16146832. https://doi.org/10.1002/aenm.201700299
[85] Ouyang L, Zhong H, Li HW, Zhu M. A recycling hydrogen supply system of $NaBH_4$ based on a facile regeneration process: a review. Inorganics 2018 Mar;6(1):10. ISSN 2304-6740. https://doi.org/10.3390/inorganics6010010
[86] Nuñez SG, Schott DL, Padding JT. Predicting the energy dissipation in a high-energy ball mill with discrete element modeling. Authorea Preprint 2024 Oct. https://doi.org/10.36227/techrxiv.172565505.54889130/v1
[87] Pierrat P, Agrawal DK, Caram HS. Effect of moisture on the yield locus of granular materials: theory of shift. Powder Technol 1998 Oct;99(3):220–27. ISSN 0032-5910. https://doi.org/10.1016/S0032-5910(98)00111-9
[88] Kalman H. Effect of moisture content on flowability: angle of repose, tilting angle, and Hausner ratio. Powder Technol 2021 Nov;393:582–96. ISSN 00325910. https://doi.org/10.1016/j.powtec.2021.08.010
[89] Cao Z, Ye X, Gu C, Cai Y, Wang J. Thermal effects on shear characteristics of unbound granular materials under drained conditions. J Geotech Geoenviron Eng 2023 Apr;149(4):04023012. https://doi.org/10.1061/JGGEFK.GTENG-10803
[90] Li HW, Yan Y, Orimo S, Züttel A, Jensen CM. Recent progress in metal borohydrides for hydrogen storage. Energies 2011 Jan;4(1):185–214. ISSN 1996-1073. https://doi.org/10.3390/en4010185
[91] Port of Rotterdam. Bunkersales 2021-2024. https://www.portofrotterdam.com/sites/default/files/2024-04/bunkersales-2021-2024.Pdf
[92] Integr8fuels. https://integr8fuels.com/
[93] IMO. Amendments to the 2014 guidelines on the method of calculation of the attained Energy Efficiency Design Index (EEDI) for new ships. https://wwwcdn.imo.org/localresources/en/KnowledgeCentre/IndexofIMOResolutions/MEPCDocuments/MEPC.281(70).pdf
[94] IEA Bioenergy. Biofuels for the marine shipping industry. https://www.ieabioenergy.com/wp-content/uploads/2018/02/Marine-biofuel-report-final-Oct-2017.pdf
[95] Schulze D. Powders and bulk solids: behavior, characterization, storage and flow. Berlin; New York: Springer; 2008. ISBN 978-3-540-73767-4.
[96] Murtomaa M, Laine E, Salonen J, Kuusinen O. On effects of ambient humidity on sodium borohydride powder. Powder Handl Process 1999 Jan;11(1).
[97] Stockmayer WH, Rice DW, Stephenson CC. Thermodynamic properties of sodium borohydride and aqueous borohydride ion. J Am Chem Soc 1955 Apr;77(7):1980–83. ISSN 0002-7863, 1520-5126. https://doi.org/10.1021/ja01612a082
[98] Beaird AM, Davis TA, Matthews MA. Deliquescence in the hydrolysis of sodium borohydride by water vapor. Ind Eng Chem Res 2010 Oct;49(20):9596–99. ISSN 0888-5885. https://doi.org/10.1021/ie100244v
[99] Kong V, Foulkes FR, Kirk DW, Hinatsu JT. Development of hydrogen storage for fuel cellgenerators. I: Hydrogen generation using hydrolysishydrides. Int J Hydrogen Energy 1999 Jul;24(7):665–75. ISSN 03603199. https://doi.org/10.1016/S0360-3199(98)00113-X
[100] Filinchuk Y, Hagemann H. Structure and properties of $NaBH_4{\cdot}2H_2O$ and $NaBH_4$. Eur J Inorg Chem 2008 Jul;2008(20):3127–33. ISSN 1434-1948, 1099-0682. https://doi.org/10.1002/ejic.200800053
[101] van Benten MC, Padding JT, Schott DL. Towards hydrogen-fuelled marine vessels using solid hydrogen carriers. In: The 14th international conference on bulk materials storage, handling and transportation, Wollongong, Australia; 2023 Jul.
[102] Gray S. Fuelling mobility: coal and Britain's naval power, c. 1870–1914. J Hist Geogr 2017 Oct;58:92–103. ISSN 03057488. https://doi.org/10.1016/j.jhg.2017.06.013
[103] Ye W. Recent developments in coal handling for terminals, stockyards and power plants. Port Technol Int 2005;25.
[104] Venkat Reddy Y, Venkatesh S. Flow characteristic evaluation of iron ore for design of bunkers and chutes with different liner materials. Mater Today Proc 2023 Jan;76:95–102. ISSN 2214-7853. https://doi.org/10.1016/j.matpr.2022.10.132
[105] Schott DL, Lodewijks G. Open versus closed storage on bulk terminals. Bulk Solids Handling 2006;26(8):540–45.
[106] Ding J, Qi C, Yan X, Lv X, Zhang S, Liang H, et al. Effect of airflow velocity on flame propagation and pressure of starch dust explosion in a pneumatic conveying environment. Powder Technol 2024 Jan;433:119147. ISSN 0032-5910. https://doi.org/10.1016/j.powtec.2023.119147
[107] Larsson SH, Lestander TA, Crompton D, Melin S, Sokhansanj S. Temperature patterns in large scale wood pellet silo storage. Appl Energy 2012 Apr;92:322–27. ISSN 0306-2619. https://doi.org/10.1016/j.apenergy.2011.11.012
[108] Stoklosa AM, Lipasek RA, Taylor LS, Mauer LJ. Effects of storage conditions, formulation, and particle size on moisture sorption and flowability of powders: a study of deliquescent ingredient blends. Food Res Int 2012 Dec;49(2):783–91. ISSN 0963-9969. https://doi.org/10.1016/j.foodres.2012.09.034
[109] NASA Earth Observatory. World's longest conveyor belt system. https://earthobservatory.nasa.gov/images/150869/worlds-longest-conveyor-belt-system, 2022 Dec.
[110] Gutierrez A, Garate G. Design of a transfer chute for multiple operating conditions. In: Volume 11: Systems, design, and complexity, Montreal, Quebec, Canada; 2014 Nov. p. V011T14A005. ISBN 978-0-7918-4960-6. https://doi.org/10.1115/IMECE2014-36414
[111] van Rheenen ES, Padding JT, Kana AA, Visser K. Ship system design changes for the transition to hydrogen carriers. Int Mar Des Conf 2024 May. ISSN 3050-4864. https://doi.org/10.59490/imdc.2024.894
[112] Ammar NR. An environmental and economic analysis of methanol fuel for a cellular container ship. Transp Res Part D Transp Environ 2019 Apr;69:66–76. ISSN 1361-9209. https://doi.org/10.1016/j.trd.2019.02.001
[113] Shakespeare CJ, Roderick ML. What controls near-surface relative humidity over the ocean? J Adv Model Earth Syst 2024. 16(6):e2023MS004168. ISSN 1942-2466. https://doi.org/10.1029/2023MS004168
[114] Takahashi H, Yasuzawa Y. Study on the effect of liquid in tanks on the hull girder vibration. In: Okada T; Suzuki K, Kawamura Y, editors. Practical design of ships and other floating structures, Singapore; 2021. p. 330–44. ISBN 978-981-15-4672-3. https://doi.org/10.1007/978-981-15-4672-3_21
[115] Tripathi R, Jadhav TA, Gaikwad MK, Naidu MJ, Gawand AB, Kaya D, et al. Vibration analysis of piping connected with shipboard equipment. Front Mech Eng 2024 May.. https://doi.org/10.3389/fmech.2024.1396170
[116] Shah DS, Moravkar KK, Jha DK, Lonkar V, Amin PD, Chalikwar SS. A concise summary of powder processing methodologies for flow enhancement. Heliyon 2023 May;9(6):e16498. ISSN 2405-8440. https://doi.org/10.1016/j.heliyon.2023.e16498.
[117] Ansari MS, Annabattula RK, Subbiah S. Gravity-driven powder flow and the influence of external vibration on flow characteristics. Particuology 2024 May;88:201–09. ISSN 1674-2001. https://doi.org/10.1016/j.partic.2023.08.023
[118] Zhang N, Rosato AD. Experiments and simulations on vibration induced densification of bulk solids. KONA Powder Part J 2006;24:93–103. https://doi.org/10.14356/kona.2006012
[119] Copernicus Marine MyOcean Viewer. https://data.Marine.copernicus.eu/viewer
[120] Hopper Screw Conveyor Dahan Machine. https://www.dahanmachine.com/product-center/Hopper-Screw-Conveyor.html.
[121] Olanrewaju TO, Jeremiah IM, Onyeanula PE. Design and fabrication of a screw conveyor. Agric Eng Int CIGR J 2017 Oct;19(3):156–62 . ISSN 1682-1130.
[122] Waje SS, Thorat BN, Mujumdar AS. Screw conveyor dryer: process and equipment design. Drying Technol 2007 Feb;25(1):241–47. ISSN 0737-3937. https://doi.org/10.1080/07373930601161112
[123] Wable MM, Kurkute VK. Design and analysis of screw conveyor at inlet of Ash/Dust conditioner. Int J Emerg Technol Adv Eng 2015 May;5(5):291–96. ISSN 22502459.
[124] Katterfeld A, Williams K. Functional analysis of tube chain conveyors Part 2: Experimental research and final recommendation for the calculation. Bulk Solids Powder-Sci Technol 2008;3(2).
[125] Katterfeld A, Williams K. Functional analysis of tube chain conveyors Part 1: General design and calculation principles. Bulk Solids Powder-Sci Technol 2008;3(1).
[126] Krause F, Katterfeld A. Functional analysis of tube chain conveyors. Part Part Syst Charact 2004 Nov;21:348–55. https://doi.org/10.1002/ppsc.200400937
[127] Schmolke S, Katterfeld A, Krause F. Experimental tests and design of tube chain conveyors. In: 7th international conference on bulk materials, storage, handling & transportation; 2001.
[128] Hrabovský L, Fries J. Transport performance of a steeply situated belt conveyor. Energies 2021 Jan;14(23):7984. ISSN 1996-1073. https://doi.org/10.3390/en14237984
[129] Zamiralova ME. Design aspects of pipe belt conveyors. 2017 May. TU Delft Repository. Retrieved from https://repository.tudelft.nl/
[130] Batwe S, Jaju S, Vaidya S. Pipe conveyor. Int Res J Eng Technol 2017 Nov;4(11). ISSN 2395-0056.
[131] Lodewijks G, Pang Y. Pipe belt conveyor systems: an update on operational performance. In: ICBMH2023: 14th international conference on bulk materials storage, handling and transportation, Wollongong, NSW; 2023.

[132] Žídek M, Zegzulka J, Jezerska L, Hlosta J, Necas J. Optimisation of geometry of the chain conveyor carriers by DEM method. Inż Miner 2015.
[133] Žídek M, Rozbroj J, Jezerska L, Diviš J, Nečas J, Zegzulka J, et al. Effective use of DEM to design chain conveyor geometry. Chem Eng Res Des 2021 Mar;167:25–36. ISSN 0263-8762. https://doi.org/10.1016/j.cherd.2020.12.017
[134] Bradley MSA. Pneumatic conveying [class handout]. Wolfson Centre for Bulk Solids Handling Technology, University of Greenwich; 2023.
[135] Bakhshipour A, Rahmanian-Koushkaki H. Chapter Ten - pneumatic conveyors. In Jafari SM, Malekjani N, editors. Transporting operations of food materials within food factories. Woodhead Publishing; 2023 Jan. p. 265–91. ISBN 978-0-12-818585-8. https://doi.org/10.1016/B978-0-12-818585-8.00004-0
[136] Gomes de Freitas A, Furlan de Oliveira V, Oliveira Lima Y, Borges dos Santos R, Alberto Martinez Riascos L. Energy efficiency in pneumatic conveying: performance analysis of an alternative blow tank. Part Sci Technol 2021 Oct;39(7):868–76. ISSN 0272-6351. https://doi.org/10.1080/02726351.2020.1850574
[137] Zhu H, Xu H, Zhong W, Yu A. Experimental study on conveying characteristics of a novel top-discharge blow tank for fine cohesive powders. Powder Technol 2021 Feb;379:335–44. ISSN 0032-5910. https://doi.org/10.1016/j.powtec.2020.10.033
[138] Rhodes MJ. Introduction to particle technology. 2nd ed. Chichester, England; Hoboken, NJ: Wiley; 2008. ISBN 978-0-470-72710-2.
[139] Molnar V, Fedorko G, Stehlikova B, Paulikova A. Influence of tension force asymmetry on distribution of contact forces among the conveyor belt and idler rolls in pipe conveyor during transport of particulate solids. Measurement 2015 Mar;63:120–27. ISSN 0263-2241. https://doi.org/10.1016/j.measurement.2014.12.014
[140] Owen PJ, Cleary PW. Prediction of screw conveyor performance using the Discrete Element Method (DEM). Powder Technol 2009 Aug;193(3):274–88. ISSN 0032-5910. https://doi.org/10.1016/j.powtec.2009.03.012
[141] Owen PJ, Thorat N, Mujumdar AS. Screw conveyor dryer: process and equipment design; 2007. https://www.tandfonline.com/doi/epdf/10.1080/07373930601161112?needAccess=true&role=button.
[142] Ananth KNS, Rakesh V. Design and selecting the proper conveyor-belt. Int J Adv Eng Technol 2013 Jun;4(2):7.
[143] McKee SL, Dyakowski T, Williams RA, Bell TA, Allen T. Solids flow imaging and attrition studies in a pneumatic conveyor. Powder Technol 1995 Jan;82(1):105–13. ISSN 00325910. https://doi.org/10.1016/0032-5910(94)02894-T
[144] Teunou E, Fitzpatrick J. Effect of storage time and consolidation on food powder flowability. J Food Eng 2000 Feb;43(2):97–101. ISSN 0260-8774. https://doi.org/10.1016/S0260-8774(99)00137-5
[145] Kalman H. Particle breakage and attrition. KONA Powder Part J 2000;18:108–20. https://doi.org/10.14356/kona.2000017
[146] Seiphoori A, Duong TNM, Geyin M. A mechanistic understanding of interface shear behavior of cohesionless materials using torsional ring shear test. In: Proceedings of the 3rd Vietnam symposium on advances in offshore engineering; 2024.
[147] Louati H, Oulahna D, de Ryck A. Effect of the particle size and the liquid content on the shear behaviour of wet granular material. Powder Technol 2017 Jun;315:398–409. ISSN 0032-5910. https://doi.org/10.1016/j.powtec.2017.04.030
[148] Fitzpatrick J, Iqbal T, Delaney C, Twomey T, Keogh MK. Effect of powder properties and storage conditions on the flowability of milk powders with different fat contents. J Food Eng 2004 Oct;64(4):435–44. ISSN 0260-8774. https://doi.org/10.1016/j.jfoodeng.2003.11.011
[149] Garg V, Deng T, Bradley MSA. A new method for assessing powder flowability based on physical properties and cohesiveness of particles using a small quantity of samples. Powder Technol 2022 Jan;395:708–19. ISSN 0032-5910. https://doi.org/10.1016/j.powtec.2021.10.027
[150] Ganesan V, Rosentrater KA, Muthukumarappan K. Flowability and handling characteristics of bulk solids and powders – a review with implications for DDGS. Biosyst Eng 2008 Dec;101(4):425–35. ISSN 1537-5110. https://doi.org/10.1016/j.biosystemseng.2008.09.008
[151] Weinhart T, Fuchs R, Staedler T, Kappl M, Luding S. Sintering—Pressure- and temperature-dependent contact models. In Antonyuk S, editor. Particles in contact: micro mechanics, micro process dynamics and particle collective. Cham: Springer International Publishing; 2019. p. 311–38. ISBN 978-3-030-15899-6. https://doi.org/10.1007/978-3-030-15899-6_10
[152] Ghellab T, Charifi Z, Baaziz H, Latteli H, Güler M, Uğur Ş, et al. The elastic, mechanical, and thermodynamic properties of NaXH4 (X = B, Al) intended for the storage of hydrogen: an ab-initio study. Physica B Condens Matter 2022 Aug;638:413851. ISSN 0921-4526. https://doi.org/10.1016/j.physb.2022.413851
[153] Basu S, Diwan M, Abiad MG, Zheng Y, Campanella OH, Varma A. Transport characteristics of dehydrogenated ammonia borane and sodium borohydride spent fuels. Int J Hydrogen Energy 2010 Mar;35(5):2063–72. ISSN 03603199. https://doi.org/10.1016/j.ijhydene.2009.12.159
[154] Muradov N. An energy-dense Al-$NaBH_4$-PEMFC based power generator for unmanned undersea vehicles. 2016 Mar. US Defence Technical Information Center. Retrieved from https://apps.dtic.mil/sti/citations/AD1007683