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Van Rheenen, E.S.; Padding, J.T.; Visser, K.

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# A 0D Model for the Comparative Analysis of Hydrogen Carriers in Ship's Integrated Energy Systems

E.S. van Rheenen<sup>a,\*</sup>, J.T. Padding<sup>a</sup>, and K. Visser<sup>a</sup>

<sup>a</sup>Delft University of Technology, Delft, The Netherlands  
\*E.S.vanRheenen@tudelft.nl

## Abstract

Hydrogen carriers are attractive alternative fuels for the shipping sectors. They are zero-emission, have high energy densities, and are safe, available, and easy to handle. Sodium borohydride, potassium borohydride, dibenzyltoluene, n-ethylcarbazole, and ammoniaborane are interesting hydrogen carriers, with high theoretical energy densities. The exact energy density of these hydrogen carriers depends on the integration of heat and mass with the energy converters. This combination defines the energy efficiency and, thus, the energy density of the system. Using a 0D model, we combined the five carriers with two types of fuel cells (PEM and SOFC), an internal combustion engine and a gas turbine. This resulted in 20 combinations. Despite the limitations of the 0D model and the occasional difficulty of validating input values, this model still produces exciting findings, which are valuable for further research. For the dehydrogenation of both dibenzyltoluene and n-ethylcarbazole, an external hydrogen burner is required if no waste heat resources from the integrated system are available. For the borohydrides, on the other hand, energy integration is essential for reducing cooling power. Dehydrogenation produces substantial energy, but only a fraction of this energy can be used for internal preheating. Dehydrogenation of ammoniaborane produces less energy. Among all hydrogen carriers, both ammoniaborane and sodium borohydride provide energy densities comparable to that of marine diesel oil. In particular, ammoniaborane possesses a remarkably high energy density. Thus, we conclude, that hydrogen carriers are attractive alternative fuels that deserve more attention, including their potential performance for hydrogen imports.

**Keywords:** Alternative fuel; Energy analysis; Hydrogen carrier; Hydrogen generation.

## 1 INTRODUCTION

The shipping sector, which uses oil-based fuels, emits 3% of global greenhouse gases [1]. Currently, the sector is not on track to reach net-zero greenhouse gas emissions by 2050 [1], [2]. Alternative low- and zero-carbon fuels such as ammonia, methanol, LNG and hydrogen, are considered as convenient methods of reduction [3]. The diversity of ship types makes it impossible for a single alternative fuel to meet all of their requirements for now. Ammonia and methanol are toxic. Methanol and LNG still emit CO<sub>2</sub> and other harmful emissions, and LNG is a fossil fuel, making it unsustainable. Gaseous hydrogen has a low volumetric energy density and pure hydrogen is extremely flammable. However, hydrogen is the only fuel with zero-emission performance as it emits only water when used. The major issues with hydrogen, the low energy density and high flammability, can be resolved by storing hydrogen in hydrogen carriers. Hydrogen carriers are liquid or solid substances that can store and release hydrogen when required. They store hydrogen by chemically bonding it or adsorb-

ing it into their structure. Thus, no hydrogen gas is present onboard anymore. We previously identified five hydrogen carriers that meet the before-mentioned requirements: two liquid organic hydrogen carriers (LOHCs): N-ethylcarbazole (NEC) and dibenzyltoluene (DBT) and three boron-based carriers: NaBH<sub>4</sub>, KBH<sub>4</sub>, and ammoniaborane [4]. However, we only evaluated whether these hydrogen carriers comply with the requirements on a theoretical level. In contrast, the energy density of these hydrogen carriers depends on much more than just the theoretical energy density. Examples include packing factors, different densities depending on particle size and energy loss in the dehydrogenation process. Most research focuses only on LOHCs combined with fuel cells and is not in a maritime context [5]–[9]. Only one study, focusing on KBH<sub>4</sub> conducted an integration within a maritime context [10].

This study aims to obtain the practical density values of the previously identified hydrogen carriers when the dehydrogenation process is included. Our study will utilize a zero-dimension integration model of the five before-mentioned hydrogen carriers combined with four different energy converters to find

the efficiency of the combinations. The practical energy density of the different hydrogen carrier and energy converter combinations follows from this efficiency. This contribution will give insight into which hydrogen carriers should be considered as alternative fuels in the maritime industry.

## 2 SELECTION OF HYDROGEN CARRIERS AND ENERGY CONVERTERS

Table 1: Theoretical volumetric and gravimetric energy densities of hydrogen carriers for explicit application onboard ships[4]

Carrier	MJ/kg	MJ/L
Ammoniatorane	23.52	14.4
NaBH <sub>4</sub> (hydrolysis)	25.56	27.34
KBH <sub>4</sub> (hydrolysis)	17.76	20.78
LOHC: NEC	6.98	6.63
LOHC: DBT	7.44	7.0
MDO	29	30

We consider five different hydrogen carriers, namely two LOHCs (DBT and NEC), two borohydrides (NaBH<sub>4</sub> and KBH<sub>4</sub>) and ammoniatorane. These hydrogen carriers fulfil the aforementioned requirements to a certain extent. As energy converters, that is the machines that convert chemical energy into either electrical or mechanical energy, we consider four different types. On the one hand we look at conventionally used energy converters such as internal combustion engines (ICE) and gas turbines (GT) and on the other hand at innovative fuel cells, specifically solid oxide fuel cells (SOFC) and proton exchange membrane fuel cells (PEMFC).

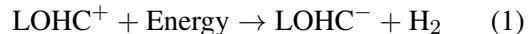
### 2.1 Hydrogen carriers

In this section, we will give a very short description of the used hydrogen carriers (of which an overview including the energy densities can be seen in table 1) and specific properties that are needed to calculate the overall efficiency of a hydrogen carrier-energy converter system, such as the energy required for dehydrogenation. For a more thorough description of hydrogen carriers and the corresponding references, as well as more detailed selection criteria, we refer to [4].

#### 2.1.1 LOHCs

DBT and NEC are chosen because DBT has one of the highest energy densities of LOHCs and NEC

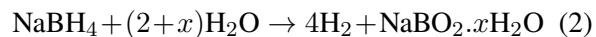
has a relatively low release temperature. LOHCs release hydrogen endothermically, at elevated temperatures. Equation 1 shows the general release mechanism of LOHCs.



The exact release temperature depends on the LOHC and the corresponding catalyst. For DBT, the temperatures lie between 553 and 593K and, for NEC, the temperatures lie between 453 and 523K [8]. The dehydrogenation and decomposition temperatures of DBT are similar, requiring careful heat control and possible gaseous stream cleanup. Additionally, external heat may be required for complete dehydrogenation. NEC has better dehydrogenation kinetics [8], [11]. However, its spent fuel is solid at room temperature, requiring continuous heating until it enters the tank.

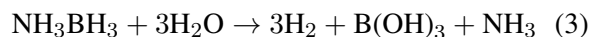
#### 2.1.2 Borohydrides and ammoniatorane

Ammoniatorane, NaBH<sub>4</sub>, and KBH<sub>4</sub> are solid powders with similar chemical properties at ambient conditions, including a high theoretical density and hydrogen release through hydrolysis. The release of hydrogen through hydrolysis with the borohydrides (NaBH<sub>4</sub> and KBH<sub>4</sub>) is very similar, taking the example of NaBH<sub>4</sub>:



The reaction is exothermic; energy is released during the dehydrogenation process and thus cooling is required. A drawback of borohydrides is that the spent fuel is heavier than the fuel. Because the weight of the spent fuel depends on the exact dehydrogenation reaction, it is not considered here.

The dehydrogenation mechanism of ammoniatorane is very similar, although it forms different products. Equation 3 describes the dehydrogenation reaction.



However, next to the metaborate, the hydrolysis reaction also produces the toxic gas ammonia. This gas can either be burned in a heat engine, decomposed into N<sub>2</sub> and H<sub>2</sub> for use in a fuel cell or stored on board. The final option is considered impractical for ships because it requires a completely different, additional, storage system, significantly reducing the energy density of the system. This study disregards the second option (cracking) due to its complexity and additional space requirements. Thus, in this study, we will work with the resulting mixture of H<sub>2</sub> and NH<sub>3</sub> as input fuel for the energy converters when using ammoniatorane.

## 2.2 Energy converters

Energy converters are defined as devices that convert chemical energy into either electrical or mechanical energy. Ships typically use compression ignition ICEs, but these have challenges when using hydrogen as a single fuel due to its high auto ignition temperature. Thus, the sector is considering alternative energy converters, such as spark ignition ICE and fuel cells. We have identified four promising energy converters for the maritime sector: spark ignition ICEs, gas turbines (GTs), PEMFCs and SOFCs. Spark ignition ICEs are similar to current engines, while GTs have been used on ships previously due to their high power density [12]. Both can be run on alternative fuels such as hydrogen, and their high outlet temperatures make them suitable for heat integration. Fuel cells have gained attention because of their modularity and high efficiency. PEMFCs are low-temperature fuel cells that require pure hydrogen, whereas SOFCs operate at much higher temperatures and are less sensitive to poisoning. Both have high efficiencies, but only produce electricity, so an electrical conversion system is required.

## 3 MODEL

To assess the efficiency and thus the total energy density of the hydrogen carrier, we constructed a simplified 0D thermodynamic model. The electricity or mechanical energy produced in the energy converter is not converted to the same type of power output to keep the playing field as level as possible. Each energy converter converts energy the way they are the most efficient.

### 3.1 Endothermic model

Fig. 1 shows the basic model of an endothermic-release hydrogen carrier system. The system has an additional heat exchanger set that uses heat from the coolant, spent fuel, and exhaust to preheat the LOHC. Heat from the exhaust is used for the final preheating and dehydrogenation of the LOHC. If more heat is required, a hydrogen burner with an efficiency of 90% is used. The hydrogen required for the burner is tapped off before it reaches the energy converter.

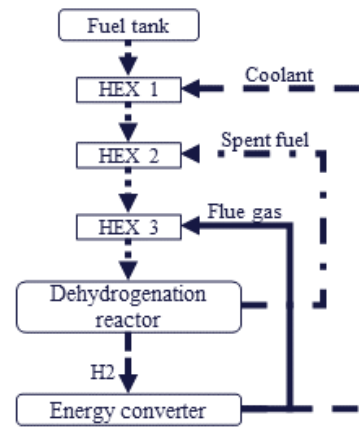


Figure 1: Simplified display of the endothermic model. HEX stands for heat exchanger

### 3.2 Exothermic model

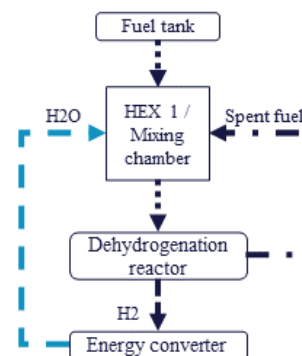


Figure 2: Simplified display of the exothermic model. HEX stands for heat exchanger

The exothermic model has a single heat exchanger that also serves as the mixing chamber. The heat exchanger is heated with the spent fuel, which has sufficient energy and also needs to be cooled down. Ammonia is poisonous to PEMFCs, therefore we do not consider this energy converter for ammonia-borane.

### 3.3 Input values for model

Table 2 gives an overview of the parameters used in the energy converter section of the model and table 3 shows the parameters used in the dehydrogenation reactor, preheating and mixing chamber sections of the model.

Table 2: Parameters of energy converters including sources.

Parameter	SI-ICE	PEMFC	SOFC	GT
T coolant [K]	363	348	0	0
P coolant [%]	30	44.8	0	0
P effective [%]	35	42.9	48	37.5
T flue gas [K]	623*	0	1023	790
P flue gas [%]	25	0	42.1	29
P losses [%]	10	12.3	9.9	33.5
Sources	[13]	[14]	[15]	[16], [17]

With P percentages of overall power distribution, mainly based on Sankey diagrams.

\* Flue gas temperature of SI-ICE largely fluctuates depending on operating conditions and can range from 423 to 773K

Table 3: Parameters of hydrogen carriers

Parameter	DBT	NEC	NaBH <sub>4</sub>	KBH <sub>4</sub>	Ammonia-borane
Hydrogen yield per molecule of hydrogen carrier [-]	9	6	4	4	3
Molecular weight [g/mol]	290.54	207	37.8	53.94	30.8
Heat capacity fuel (pure) [kJ/kgK]	1.58	1.49	2.23	1.2	2.7
Heat capacity spent fuel (pure) [kJ/kgK]	1.49	1.50	0.6221	1.0512*	0.7937*
Dehydrogenation temperature [K]	573	503	333	333*	333*
Dehydrogenation energy [kJ/mol Fuel]	558	318	-210	-21	-220
Sources	[6], [18]	[19]–[21]	[22]–[24]	[25]	[26], [27]

Values denoted with \* are estimated by the authors as no precise information was available

For the SOFC we have set the cooling to zero, as in the model this is treated as low-temperature cooling. SOFCs are air-cooled, at relatively high temperatures. This cooling is called "flue gas" in the model. For the overall heat capacity of mixtures, we calculate the heat capacity using the rule of mixtures. We assume 100% conversion. In instances where precise or accurate data was not available, estimated values were derived based on analogous processes or chemical structures.

Unfortunately, sources looking at ammonia-hydrogen dual-fuel options usually consider only a small amount of hydrogen and can thus not be directly used. However, no alterations are considered in terms of overall efficiencies or outlet temperatures for the mixture of ammonia and hydrogen compared to hydrogen only. This assumption is based on the substantial quantity of hydrogen present in the feed (75% mole fraction which contributes approximately 70% of the total energy) and the similarity of the efficiencies of hydrogen only and ammonia

only [15], [28].

## 4 RESULTS AND DISCUSSION

This section provides an overview and a discussion of the results of the model. Subsection 4.1 provides a validation of the results, while subsection 4.2 gives an overview of the efficiency and distribution of energy of the whole cycle, including the dehydrogenation process. The hydrogen carrier quantity necessary for a 5000kW power output and its corresponding energy distribution are discussed in subsection 4.3. Additionally, subsection 4.4 gives an overview of required additional water to the system in the case of borohydrides, depending on the efficiency of the recycling system. Finally, subsection 4.5 gives the effective energy densities for each of the systems, compared to MDO, and subsection 4.6 discusses the limitations of the model and provides recommendations for further research.

### 4.1 Validation of results

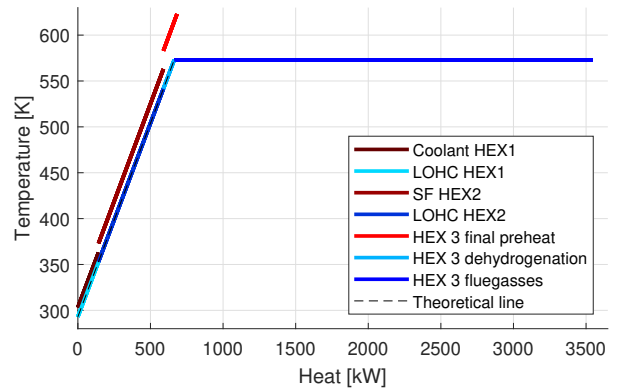


Figure 3: Pinch analysis of heat exchangers with DBT and ICE

To verify whether the results are physically possible, we performed a pinch analysis on each of the total heat-exchanging systems. Fig. 3 gives an example of such a pinch analysis. The pinch analysis shows the hot and cold flows, their temperatures and the amount of heat they contain. A physically possible process will never have the hot and cold flows cross within a pinch analysis, because the hot flows must always remain hotter than the cold flows for heat transfer to occur. Fig. 3 confirms that this is the case for the analyzed systems.

### 4.2 Energy efficiency analysis

The energy analysis, represented in Fig. 4 to 7 shows the energy distribution throughout the sys-

tem, organised per hydrogen carrier. These figures show the delivered power, energy in the coolant and in the flue gases, additional energy added through a burner and absolute or irrecoverable losses that are unavoidable.

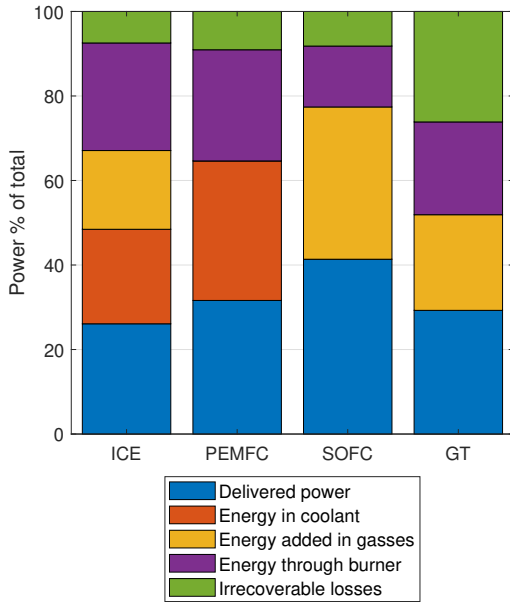


Figure 4: Efficiency and heat distribution as percentage of total available energy for DBT

Fig. 4 shows the LOHC DBT coupled to four different energy converters. Irrespective of the energy converter, an additional burner is always necessary when using DBT as a hydrogen carrier. As expected, the energy added through the burner is higher for systems operating at lower temperatures. A similar trend can be seen for NEC, (Fig. 5). However, the overall heating requirements are lower for NEC than for DBT, therefore, the amount of energy added through the burner is also lower. Even when using an SOFC or GT, a burner is still necessary to provide the heat required for the dehydrogenation process. Despite the higher heating requirements for DBT, the overall efficiency is still higher compared to NEC, due to the higher hydrogen content of DBT.

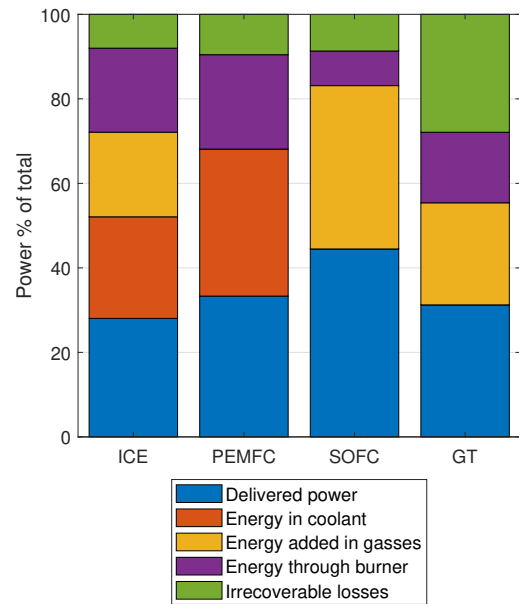


Figure 5: Efficiency and heat distribution as percentage of total energy for NEC

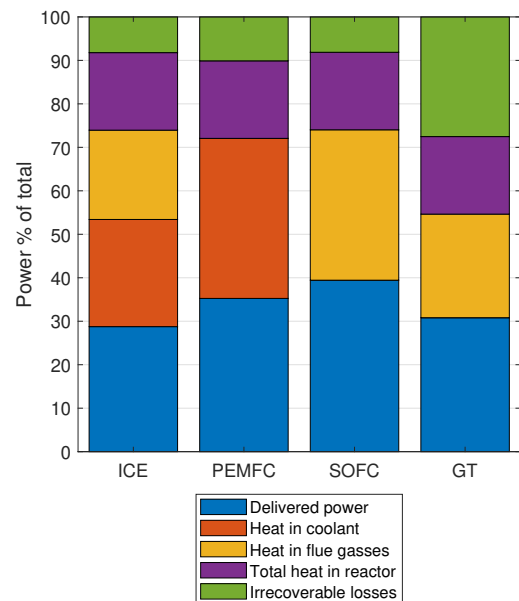


Figure 6: Efficiency and heat distribution as percentage of total energy for NaBH<sub>4</sub>

The hydrolysis reaction of borohydrides produces additional energy, which can be used to pre-heat the fuel and reduce the external cooling requirements. To avoid overheating, the reactor must be cooled constantly. It should be noted that the total heat in the reactor for both NaBH<sub>4</sub> and KBH<sub>4</sub> includes the premixing, dehydrogenation and spent fuel heat, and is reduced due to the preheating. Section 4.3 goes into more detail on this, but it is important to consider the cooling requirement when designing a system using borohydrides.

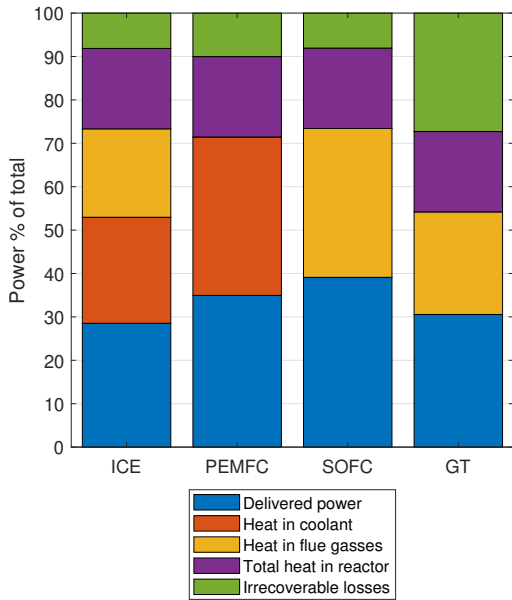


Figure 7: Efficiency and heat distribution as percentage of total energy for KBH<sub>4</sub>

The heat produced in the reactor is percentage-wise less for ammoniaborane, compared to the heat produced in the coolant and the flue gases (see Fig. 8). The combination of NH<sub>3</sub> and H<sub>2</sub> produces more power in an absolute sense, thus reducing the relative heat produced by the reactor. The percentage of power that goes to useful power is significantly higher than that of NaBH<sub>4</sub> or KBH<sub>4</sub>.

### 4.3 Detailed use of heat

Figs 9 to 12 show a detailed heat and power distribution, for a similar output power (5000kW). The resulting mass flows are listed in table 4.

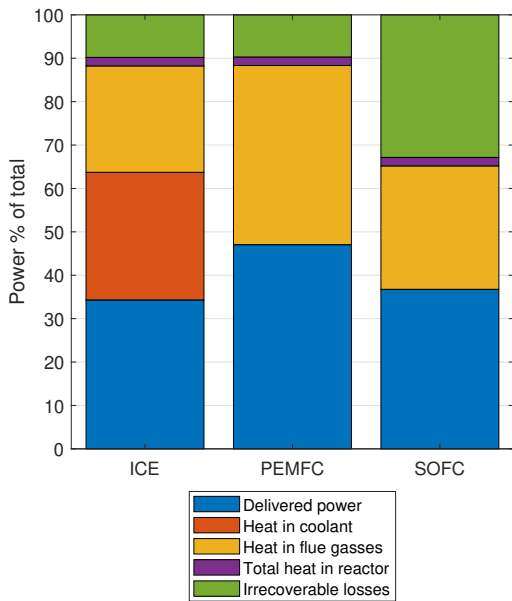


Figure 8: Efficiency and heat distribution as percentage of total energy for ammoniaborane

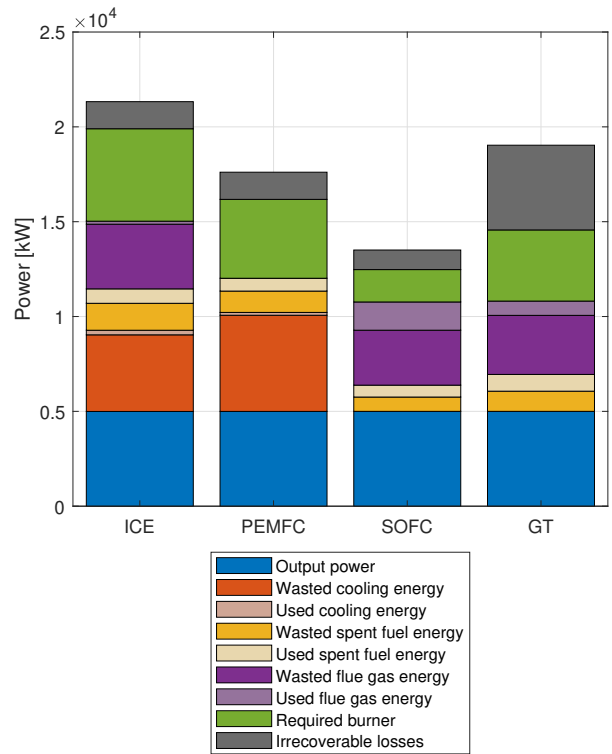


Figure 9: Detailed distribution of heat and energy in the whole system. Hydrogen carrier is DBT

Unused heat is often present in heat integration, although it is undesirable. Low-temperature heat is more difficult to use than high-temperature heat. Preheating relies on lower-temperature heat sources to make optimal use of these heat sources.

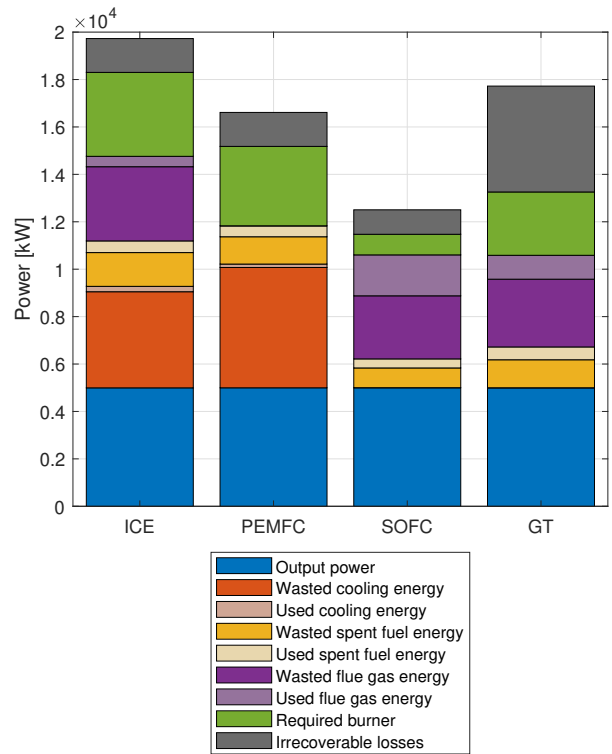


Figure 10: Detailed distribution of heat and energy in the whole system for NEC

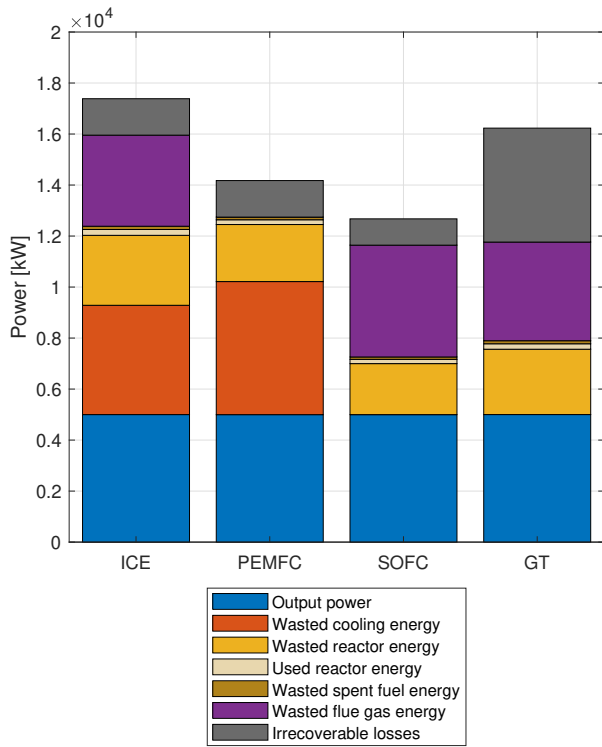


Figure 11: Detailed distribution of heat and energy in the whole system. The hydrogen carrier is  $\text{NaBH}_4$

Figs 9 and 10 show the unused heat in coolants and flue gases. Flue gas heat is the only heat available for dehydrogenation, but not all of it can be used because it can only be cooled down to the dehydrogenation temperature.

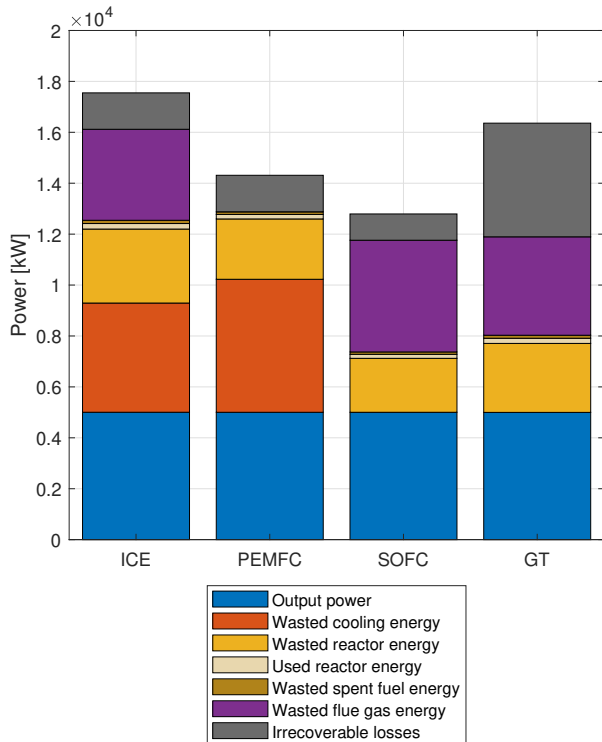


Figure 12: Detailed distribution of heat and energy in the whole system. The hydrogen carrier is  $\text{KBH}_4$

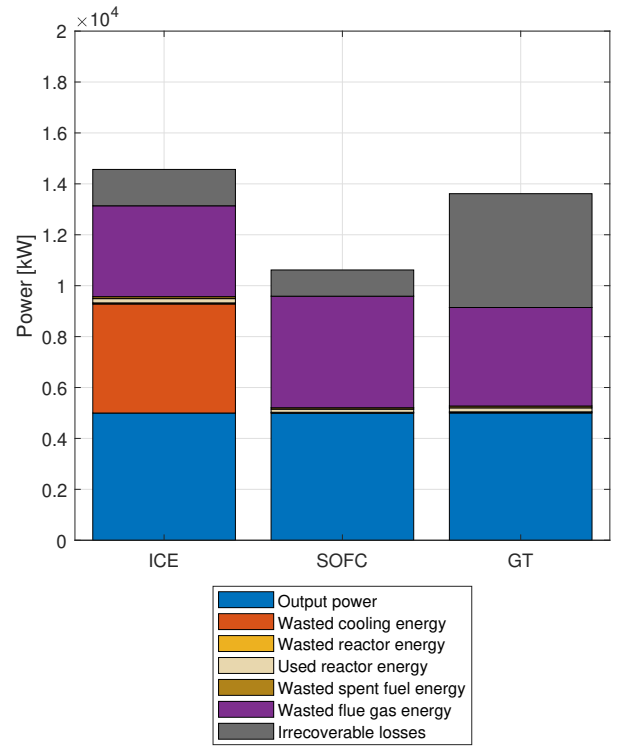


Figure 13: Detailed distribution of heat and energy in the whole system. The hydrogen carrier is ammoniaborane

Boron-based carriers yield higher power outputs. However, as only a small fraction of the reactor's energy can be used for preheating, active cooling is necessary, reducing the overall power output.

Table 4 shows the different mass flows required to reach the 5000kW. It is clear from this table that there is very little difference in the LOHCs, as the different energy densities are countered by the different dehydrogenation requirements. Additionally,  $\text{NaBH}_4$  requires less mass flow than  $\text{KBH}_4$ , irrespective of the energy converter and ammoniaborane requires the least mass flow, with differences of up to 6 times less mass flow compared to the LOHCs.

Table 4: Mass flows [kg/s] required to reach 5000kW output

Parameter	H2-ICE	PEMFC	SOFC	GT
DBT	2.56	2.11	1.62	2.28
NEC	2.54	2.14	1.61	2.82
$\text{NaBH}_4$	0.56	0.46	0.41	0.52
$\text{KBH}_4$	0.78	0.65	0.58	0.74
Ammoniaborane	0.42		0.30	0.39

#### 4.4 Additional water requirements

The hydrolysis dehydrogenation reaction requires water. Theoretically, this water could be recycled from the outlet of the energy converter and



could satisfy the overall water requirements completely for all boron-based hydrogen carriers. However, as this recycling is most likely not 100%, we examined the amount of water required for different recycling rates. Fig. 14 shows the different recycling rates. For borohydrides, it is likely that an external pure water source is needed, because if the recycling is less than 100%, additional water is necessary. For ammoniaborane, however, this external water source is only necessary for less than 75% of water recycling. This is because the conversion of hydrogen and ammonia both result in water.

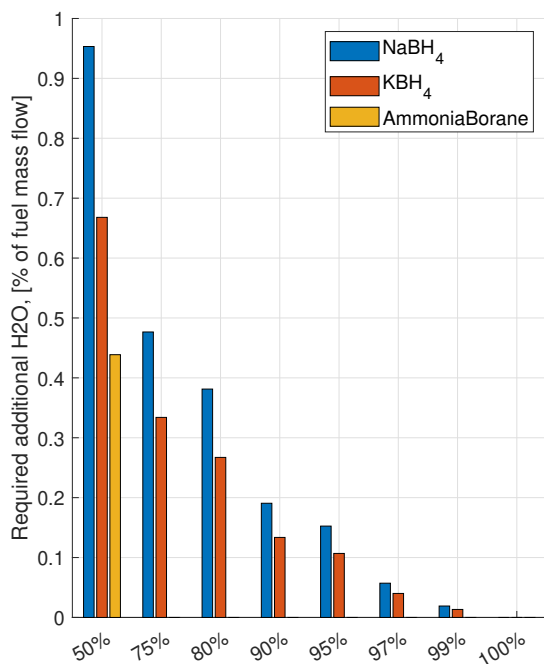


Figure 14: Effect of the water recirculation rate of water from exhaust gases on the amount of water that needs to be added to the system from an external source.

#### 4.5 Effective energy density

Fig 15 shows the effective energy density of each fuel. The effective energy density is the amount of effective mechanical or electrical energy that can be taken out of 1 kg of fuel. This definition includes the energy converter, as heat and mass integration is necessary for the efficient use of hydrogen carriers. Additionally, from fig. 15, we can conclude that there is very little difference between the LOHCs after heat integration. This suggests that the choice of LOHC may not be as important as the efficiency of the energy converter. Fig 15 also highlights the high potential of NaBH<sub>4</sub> and ammoniaborane, as these can reach effective energy densities close to that of MDO.

#### 4.6 Model limitations and further research

The current model provides a simplified, but well-founded, overview of the energy efficiency and density of the different combinations of hydrogen carriers and energy converters. This overview could be improved with more specific temperature and heat distributions of the energy converters, as well as by looking at load factors. These parameters largely depend on the operating conditions and the power requirements of ships, making them different for different ship types and different operational profiles.

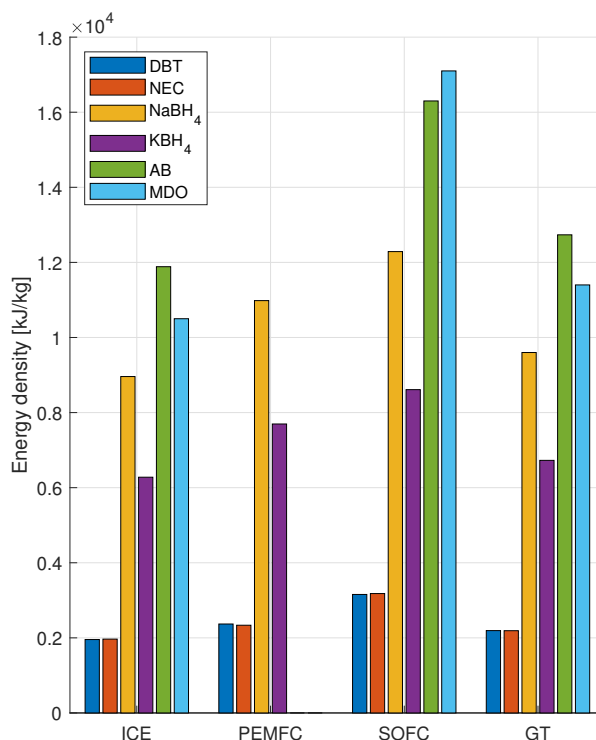


Figure 15: Effective energy density of hydrogen carriers compared to MDO for each of the energy converters. Data for MDO conversion from [15], [16]

In addition to the energy density, the power density is also important for all ships. To provide a more complete overview, the power density of each of the options should be evaluated. However, the technology readiness levels of the hydrogen carriers are not yet sufficient for this power density analysis. Besides power density, other properties of hydrogen carriers influence the possible use of fuel, such as safety, handling, availability and costs, the latter of which is closely related to the recycling process of the spent fuel.

Moreover, for borohydrides, the additional weight of the spent fuel must be considered. The spent fuel is much heavier (up to 3.7 times) than the original

fuel. To calculate the effective energy density regarding the weight and volume onboard a ship, the weight (and volume) difference should be taken into account.

The model can be enhanced for more detailed results. In the exothermic model, cooling of waste heat is currently not considered, even though cooling pumps will cost power. Using this waste heat for other purposes, such as co-generation or hotel loads can also enhance the energy efficiency of the system, particularly for boron-based carriers. Additionally, the cracking of ammonia could be considered. It would also add the PEMFC as an option for ammoniaborane. The endothermic model could be enhanced by optimizing the heat integration, as done in [7]. They demonstrated that a burner is not always necessary for endothermic hydrogen carriers. Thus, a better heat integration in our model would be advisable. However, all combined, the model provides a good first overview of the possibilities that hydrogen carriers and energy converters can provide.

## 5 CONCLUSION

The objective of this study was to evaluate the effective energy density of hydrogen carriers as alternative fuels. We accomplished this goal by examining the efficiency of the overall energy cycle when using alternative fuels. Our model can calculate different efficiencies in a simple, yet accurate manner, enabling us to draw conclusions on the efficiency and thus, on the practicability of hydrogen carriers.

The model consists of two main types, as the dehydrogenation process can be either endothermal or exothermal. However, this dehydrogenation process always requires either energy (in the form of heat) or mass (e.g. water). To determine the overall energy density of the system, we built a thermodynamic OD model which integrates the heat and mass flows of the system. This model provided a first indication of the overall energy densities of five hydrogen carriers combined with four energy converters, which are as follows.

First, the high efficiency of the SOFC makes it a compelling energy converter, independent of the alternative fuel source. Of the hydrogen carriers, the following have the highest energy densities:  $\text{NaBH}_4$  and ammoniaborane. Without taking the spent fuel into account, these energy densities are close to (and may in some cases, even surpass) the energy density of diesel. Although both LOHCs have lower energy

densities, other characteristics may still make them interesting.  $\text{KBH}_4$ , on the other hand, is not as favourable as  $\text{NaBH}_4$ .

Our study highlights the importance of heat and mass integration of hydrogen carriers and energy converters for the overall energy density. Although the OD model only provides estimates, it shows interesting findings, which should be investigated in more detail in future research. Hydrogen carriers can achieve overall energy efficiencies similar to those of conventional fuels, thereby considerably enhancing the attractiveness of more sustainable options.

## ACKNOWLEDGEMENTS

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