Electronic Supplementary Information

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Dimethyl ether/CO₂ - a hitherto underestimated H₂ storage cycle

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Process simulations using Aspen plus®

Ammonia synthesis and comparison to other vectors

For NH₃, the demand is based on own process simulation of a conventional Haber-Bosch loop supported by air separation unit (ASU) using Aspen plus[®]. For that the specific demand were extracted from a previous study were the following components were evaluated.

The ASU designed within the previous study was assumed to operate at full load in a steady state operation mode (i.e. 8000 h/a), as dynamic load variation of distillation processes would be a major technological challenge. The produced mass flow of $N_{\rm 2}$ was evaluated according to the demand of an NH₃ plant to produce 300 daily tonnes. No further usage of the side products argon (Ar) and oxygen (O₂) of the ASU was considered in this study. Therefore, the air separation process could be realized within a single-column plant design with lower complexity and equipment cost [18]. This design leads to the production of a pure N_2 stream and an enriched O_2 stream (with rest N₂ and Ar). In the ammonia synthesis section N₂ and H₂ react towards ammonia based on the equilibrium reaction. Within the previous study a synthesis pressure of 250 bar and a synthesis temperature of 550 $^\circ \! C$ were selected (Haber-Bosch process). Ammonia synthesis was implemented as a loop process with recycle stream. The reaction gas mixture containing N_2 and H_2 in stoichiometric ratio was introduced to the reactor unit to produce ammonia. Ammonia is then separated from the unreacted gases by condensation. The recycled gas is mixed with the fresh feed stream. Aspen Plus[®] V10 from Aspen Tech was used for simulating the ASU and the NH₃ synthesis.

The state-of-the-art synthesis conditions for ammonia are compared to methanol and direct, as well as indirect dimethyl ether synthesis in Table S1.

Reforming processes	of	DME,	MeOH	and	NH₃
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For simple evaluation of the specific energy demand for the feed heating and reforming of the different H₂ carriers, simple simulation was developed as shown in the Figure S. For MeOH and DME, the stoichiometric H₂O and feed stream is heated using the reformer product stream and furthermore with a trim heater to reach the required reforming temperature. The reformer is simulated as a Gibbs reactor operated at ambient pressure. The product stream containing mainly CO₂ and H₂ is then cooled to 25 °C. The specific energy to reform 1 ton of X is evaluated summing up the endothermic energy demand of the reformer and the heat needed to heat or evaporate the feedstock.

For NH₃, the gaseous ammonia feedstock is heated similarly by exchanging heat with the reformer product and then introduced to the Gibbs reactor. Under the selected conditions and using this thermodynamic approach independent from real catalytic conditions, all the H₂ carriers were completely converted to H₂ and either CO₂ or N₂. The CO2 liquefaction in case of DME was evaluated by using ideal separator after the DME reformer and compressing the separated CO₂ to 8 bar and cooling the product to -50 °C.

Table S1: Conditions in state-of-the-art synthesis of ammonia, methanol and dimethyl ether.

Hydrogen carrier synthesis	Reactants for synthesis of carrier	Synthesis temperature	Synthesis pressure	Exothermicity of reaction kJ/mol carrier	Equilibrium conversion per reactor pass	Product yield in plant including recycle stream
Ammonia ¹	N2, H2	400-500 °C	200-300 bar	- 41.3	~ 15-20 %	> 98 %
Methanol ²⁻⁴	CO ₂ , H ₂	200-300 °C	50-100 bar	- 49.6	~ 20-25 %	> 94 %
Dimethod athen (DN45)257	CO ₂ , H ₂ (direct synthesis	200-300 °C	50-100 bar	- 123.2	~ 30-55 %	> 94 %
Dimethyl ether (DME) ^{2,37}	Methanol (indirect synthesis)	220-360 °C	< 20 bar	- 24.0	70-100%	> 99 %

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Table S2: Conditions and main results of reforming simulations

H ₂ carrier	MeOH	NH_3	DME
Reformer conditions			
т, [°C]	300	550	350
Pre-heater heat demand [MWh t^1 X]	0.62	0.01	0.74
Reformer heat demand [MWh t ⁻¹ X]	0.521	0.876	0.872
Net heat demand [MWh t ⁻¹ X]	1.14	0.88	1.61

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Shipping evaluation basis

Table S3: Main parameters for shipping cost evaluation

H ₂ carrier	MeOH	NH_3	DME
Volume, [m³]	140,000	84,000	84,000
Capacity X, [kt]	110.6	57.2	61.32
Transport distance, [km]	20,000		
Travel time - one-way, [d]	26		
Charge and discharge duration [d]	4		
Number of trips to deliver H ₂ required per year	5	11	7
Average speed, [km/h]		32.4	
Resulting engine continuous output, [kW SMCR]	13,400	14,200	14,200
Efficiency of main engine system		0.5	
Diesel fuel consumption, [L/km]	83		88
Total consumption, [10 ³ L/trip one way]	1664	1	763
Ship CAPEX, [mio €]	50	62	62
Ship lifetime [a]		30	
Ship availability/Utilization [%]		95/100	
Ship diesel price, [€/l]		1	
Annual X transported, [kt/a]	774.2	401.0	427.3
Cost of Transport, [€ t ⁻¹ X]	32.24	66.71	62.60



Figure S1: Exemplary representation of reforming and \mbox{CO}_2 liquefaction process simulation in Aspen Plus

Supplementary results from TEA

Table S4: Key assumptions for DME synthesis from renewable elecitricity and sea water, adapted from [40, 41].

General Assumptions	
H ₂ losses during reforming, [%]	3
CO ₂ losses during reforming/back shipping, [%]	3
System component	
Electrolyzer	
H_2O demand by electrolyzer [t H_2O t ⁻¹ H_2]	10
Specific electricity consumption [MWh _{el} t ⁻¹ H ₂]	50
DAC	
Specific electricity consumption $[MWh_{el} t^{-1} CO_2]$	0.5
Specific heat demand [MWh _{th} . t ⁻¹ CO ₂]	1.5
Water Desalination assuming multi-effect distillation (MED)	
Specific electricity consumption [kWh _{el} m ⁻³ H ₂ O]	50



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Figure S2: a,b and c) Evaluations at shipping distance of 20,000 km (a) Cost structure of MeOH production at CO_2 cost from DAC. (b) Cost structure of NH_3 production at N_2 cost from ASU (c) The cost structure for delivery of 1 ton of H_2 at the utilization point using DME as H_2 carrier in a closed DME/ CO_2 cycle as a function of CO_2 cost. (d) a comparison of the energy delivered if the same ship capacity is considered for all the three carriers.



Figure S3: a,b and c) Evaluations at Shipping distance of 10,000 km (a) Cost structure of MeOH production at CO₂ cost from DAC. (b) Cost structure of NH₃ production at N₂ cost from ASU (c) Cost structure of DME production at CO₂ cost from DAC. / (d) sensitivity study covering low and high feedstock CO₂ (High= 720 \notin /t and low = 200 \notin /t) and N₂ (High= 200 \notin /t and low = 50 \notin /t) cost influence on the cost of H₂ delivery using vector X.

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Figure S4: Simplified flowsheet of the conventional indirect route (a) starting from CO_2 and H_2 and of an intensified process based on reactive distillation (b) ⁶.

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