

## Electronic Supplementary Information

### Dimethyl ether/CO<sub>2</sub> - a hitherto underestimated H<sub>2</sub> storage cycle

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### Process simulations using Aspen plus®

#### Ammonia synthesis and comparison to other vectors

For NH<sub>3</sub>, 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<sub>2</sub> was evaluated according to the demand of an NH<sub>3</sub> plant to produce 300 daily tonnes. No further usage of the side products argon (Ar) and oxygen (O<sub>2</sub>) 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<sub>2</sub> stream and an enriched O<sub>2</sub> stream (with rest N<sub>2</sub> and Ar). In the ammonia synthesis section N<sub>2</sub> and H<sub>2</sub> react towards ammonia based on the equilibrium reaction. Within the previous study a synthesis pressure of 250 bar and a synthesis temperature of 550 °C were selected (Haber-Bosch process). Ammonia synthesis was implemented as a loop process with recycle stream. The reaction gas mixture containing N<sub>2</sub> and H<sub>2</sub> 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 NH<sub>3</sub> 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 NH<sub>3</sub>

For simple evaluation of the specific energy demand for the feed heating and reforming of the different H<sub>2</sub> carriers, simple simulation was developed as shown in the Figure S. For MeOH and DME, the stoichiometric H<sub>2</sub>O 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 CO<sub>2</sub> and H<sub>2</sub> 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 NH<sub>3</sub>, 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 H<sub>2</sub> carriers were completely converted to H<sub>2</sub> and either CO<sub>2</sub> or N<sub>2</sub>. The CO<sub>2</sub> liquefaction in case of DME was evaluated by using ideal separator after the DME reformer and compressing the separated CO<sub>2</sub> 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 <sup>1</sup>	N <sub>2</sub> , H <sub>2</sub>	400-500 °C	200-300 bar	- 41.3	~ 15-20 %	> 98 %
Methanol <sup>2-4</sup>	CO <sub>2</sub> , H <sub>2</sub>	200-300 °C	50-100 bar	- 49.6	~ 20-25 %	> 94 %
Dimethyl ether (DME) <sup>2,5,7</sup>	CO <sub>2</sub> , H <sub>2</sub> (direct synthesis)	200-300 °C	50-100 bar	- 123.2	~ 30-55 %	> 94 %
	Methanol (indirect synthesis)	220-360 °C	< 20 bar	- 24.0	70-100%	> 99 %

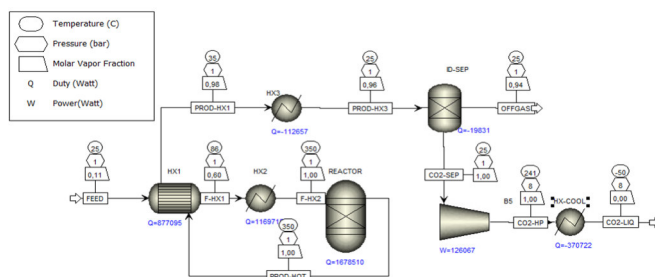
Table S2: Conditions and main results of reforming simulations

H <sub>2</sub> carrier	MeOH	NH <sub>3</sub>	DME
<b>Reformer conditions</b>			
T, [°C]	300	550	350
Pre-heater heat demand [MWh t <sup>-1</sup> X]	0.62	0.01	0.74
Reformer heat demand [MWh t <sup>-1</sup> X]	0.521	0.876	0.872
Net heat demand [MWh t <sup>-1</sup> X]	1.14	0.88	1.61

## Shipping evaluation basis

Table S3: Main parameters for shipping cost evaluation

H <sub>2</sub> carrier	MeOH	NH <sub>3</sub>	DME
Volume, [m <sup>3</sup> ]	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 <sub>2</sub> 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 <sup>3</sup> L/trip one way]	1664	1763	
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 <sup>-1</sup> X]	32.24	66.71	62.60

Figure S1: Exemplary representation of reforming and CO<sub>2</sub> liquefaction process simulation in Aspen Plus

## Supplementary results from TEA

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

General Assumptions	
H <sub>2</sub> losses during reforming, [%]	3
CO <sub>2</sub> losses during reforming/back shipping, [%]	3
System component	
Electrolyzer	
H <sub>2</sub> O demand by electrolyzer [t H <sub>2</sub> O t <sup>-1</sup> H <sub>2</sub> ]	10
Specific electricity consumption [MWh <sub>el</sub> t <sup>-1</sup> H <sub>2</sub> ]	50
DAC	
Specific electricity consumption [MWh <sub>el</sub> t <sup>-1</sup> CO <sub>2</sub> ]	0.5
Specific heat demand [MWh <sub>th</sub> t <sup>-1</sup> CO <sub>2</sub> ]	1.5
Water Desalination	
assuming multi-effect distillation (MED)	
Specific electricity consumption [kWh <sub>el</sub> m <sup>-3</sup> H <sub>2</sub> O]	50



Figure S2: a,b and c) Evaluations at shipping distance of 20,000 km (a) Cost structure of MeOH production at CO<sub>2</sub> cost from DAC. (b) Cost structure of NH<sub>3</sub> production at N<sub>2</sub> cost from ASU (c) The cost structure for delivery of 1 ton of H<sub>2</sub> at the utilization point using DME as H<sub>2</sub> carrier in a closed DME/CO<sub>2</sub> cycle as a function of CO<sub>2</sub> 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 CO<sub>2</sub> cost from DAC. (b) Cost structure of NH<sub>3</sub> production at N<sub>2</sub> cost from ASU (c) Cost structure of DME production at CO<sub>2</sub> cost from DAC. / (d) sensitivity study covering low and high feedstock CO<sub>2</sub> (High= 720 €/t and low = 200 €/t) and N<sub>2</sub> (High= 200 €/t and low = 50 €/t) cost influence on the cost of H<sub>2</sub> delivery using vector X.

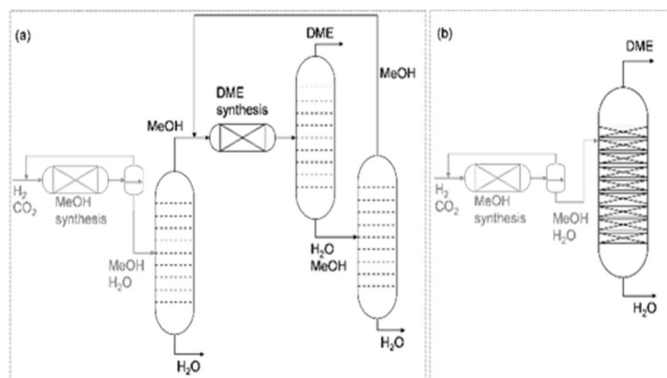


Figure S4: Simplified flowsheet of the conventional indirect route (a) starting from CO<sub>2</sub> and H<sub>2</sub> and of an intensified process based on reactive distillation (b) <sup>6</sup>.

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