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Supporting Information

Nitrogen-Based Fuels: A Power-to-Fuel-to-Power Analysis

*Alon Grinberg Dana, Oren Elishav, André Bardow, Gennady E. Shter, and Gideon S. Grader**

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1. Assumptions and energy basis

Throughout the analysis several general assumptions were made (Table S1).

Table S1. Assumptions

Number	Assumption
1	The required energy for water desalination is negligible compared to water splitting and fuels' synthesis energies.
2	Air separation, hydrogen generation and fuel production sites are in proximity to each other.
3	The energy required for storing all evaluated fuels is negligible. Moreover, only the operating energy consumptions were taken into account, while the energy for construction and decommissioning of the plants was not accounted for.
4	During the synthesis of all fuels, the required heat is assumed to be recovered within the process boundaries (the syntheses are exothermic).

The common basis chosen for the energy comparison was equivalent work (W_{eq}), defined as in Equation SE1, where E_{el} is electric energy, E_{th} is thermal energy, $\eta_{combustion}$ is taken as the combustion efficiency of methane, 54.1% (Table S2), and η_{boiler} is the boiler efficiency taken as 91%.[1]

$$W_{eq} = E_{el} + E_{th} \cdot \eta_{combustion} / \eta_{boiler} \qquad \text{(SE1)}$$

2. Combustion efficiency

The combustion efficiency is a dimensionless performance measure of the useful energy (mechanical work, heat, or possibly both) that can practically be recovered from the combustion of a given fuel. The heat content of the fuel is taken as the high heating value (HHV). The Carnot efficiency for methane combustion is 87.2%, while the current reported state of the art methane efficiency is 60% on a high heating value basis and 54.1% on a low heating value basis,[2–5] representing 69% of the theoretical Carnot value (Table S2). The same actual to theoretical efficiency ratio (i.e., 69% of the Carnot efficiency) was therefore assumed to be achieved in all other evaluated fuels. As a consequence, the estimated conversion efficiencies of all fuels are in the range of 57%–61% (Table S2). This estimation for aqueous AAN and UAN is regarded as conservative, since as monofuels they do not require compression of the air/fuel mixture in the turbo generator. Therefore, potentially, power generators based on AAN and UAN could be more efficient than standard generators based on conventional fuels.

Table S2. Combustion efficiencies for stationary power generation of the selected alternative fuels

Fuel	Adiabatic temperature (K)[a]	Carnot efficiency[b]	Actual combustion efficiency	Ratio of combustion to Carnot efficiency[c]	Estimated combustion efficiency[d]
Methane	2,327	87.2%	54.1%[e]	62%	–
MeOH	2,231	86.6%	–	62%	54%
DME	1,594	81.3%	–	62%	50%
Ammonia	2,108	85.9%	–	62%	53%
Aq. AHU	1,591	81.3%	–	62%	50%
Aq. AAN	1,234	75.9%	–	62%	47%
Aq. UAN	1,348	77.9%	–	62%	48%

[a] Calculated using standard enthalpies of formation[6] and heat capacity at constant pressure[7] for a stoichiometric feed. [b] Calculated as $(1–T_c/T_h)$,[8] where T_c=298 K and T_h is the adiabatic temperature. [c] The ratio was calculated for CH_4, and was assumed to be identical for all other fuels. [d] Calculated as the product of the Carnot efficiency and the ratio of combustion to Carnot efficiency. [e] As reported by Mitsubishi Heavy Industries LTD[2] and Siemens AG[3].

3. Energy requirement for fuel distribution

The required energy to distribute the fuels from the production site to the consumers was accounted. A distribution pathway of about 1,600 km (1,000 miles) was taken as the reference distance, resembling the distance between South California (where an abundance of solar energy could be produced) to Seattle (a center of demand). The different fuels are pressurized to 10.4 MPa similar to the maximum operating pressure for existing natural gas (NG) infrastructure currently used in the USA. The required transport energy for compressed NG (CNG) and for liquid ammonia is estimated at 1.508 GJ per ton and 0.185 GJ per ton, respectively.[9] Since all fuels in the current analysis except for methane are liquids at 10.4 MPa, the reported required energy for ammonia transport was adapted for all other liquid fuels using a volumetric density ratio (Table S3).

Table S3. Required distribution energy of the selected alternative fuel

Fluid	Density at 10.4 MPa, 25ºC (ton m^{-3})	Volumetric density ratio (ammonia to fluid)	Distribution energy (GJ ton^{-1})
Methane	0.079[a]	–	1.508[9]
MeOH	0.744[a]	0.696	0.129
DME	0.632[a]	0.820	0.152
Ammonia	0.518[a]	1	0.185[9]
Aq. AHU	0.978[10]	0.530	0.098
Aq. AAN	1.135[b]	0.456	0.084
Aq. UAN	1.330[b]	0.389	0.072
CO_2	0.826[a]	0.627	0.116

[a] Value simulated with Honeywell UniSim® Design using the Lee-Kesler-Plocker predicting method. [b] Averaged ambient pressure measured value (liquids are assumed to be non-compressible).

4. PFP^{atm} indices

Table S4 presents the parameters for the PFP calculation, energy values are in GJ ton^{-1} units.

Table S4. PFP^{atm} indices of the selected alternative fuels

Fuel	Air separation[a] (GJ ton^{-1})	Water splitting[b] (GJ ton^{-1})	Synthesis energy[c] (GJ ton^{-1})	Distribution[d] (GJ ton^{-1})	Energy density[e] (GJ ton^{-1})	Combustion efficiency[f]	PFP index[g]
Methane	18.1	90.8	1.2[11]	1.508	55.5	54%	27%
MeOH	9.1	34.1	4.8[,12]	0.129	23.7	54%	27%
DME	12.6	47.4	8.7[h]	0.152	31.7	50%	23%
Ammonia	0.18	32.1	1.6[i]	0.185	22.5	53%	35%
Aq. AHU	1.27	14.6	1.5[h]	0.098	9.2	50%	27%
Aq. AAN	0.06	11.5	0.9[h]	0.084	3.7	47%	14%
Aq. UAN	0.79	10.9	1.3[h]	0.072	3.3	48%	12%

[a] Required energy for separating N_2,[13] CO_2,[14] or both from the atmosphere as feedstock. [b] Based on a future prediction for central grid electrolysis evaluated as 180.72 GJ tonH_2^{-1}.[15] [c] Values represent state of the art required synthesis energy. [d] Calculated as in Table S3. [e] Taken as high heating value. [f] Calculated as in Table S2. [g] Calculated according to Equation E2. [h] See Sections 8, 9 of the supporting information for detailed calculations. [i] Average literature value.[9,16–18]

5. Hydrogen utilization efficiency

During fuel synthesis some of the hydrogen feedstock is not be chemically stored, but rather emitted as H_2O (amount depends on the specific fuel composition). The hydrogen utilization efficiency is given by Table S5.

Table S5. Hydrogen utilization efficiency

Fuel	Hydrogen utilization efficiency
Methane	50%[a]
MeOH	67%[b]
DME	50%[c]
Ammonia	100%[d]
Aq. AHU	90%[e]
Aq. AAN	75%[f]
Aq. UAN	67%[g]

[a] The Sabatier reaction: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. [b] Reverse water gas shift reaction, followed by methanol production from synthesis gas: $CO_2 + H_2 \rightarrow CO + H_2O$, $CO + 2H_2 \rightarrow CH_3OH$. [c] Produced by methanol dehydration. [d] The Haber-Bosch process: $1.5H_2 + 0.5N_2 \rightarrow NH_3$. [e] For the AH : urea ratio of 1 : 0.22, 1.44 moles of ammonia are required (equivalent to 4.32 moles of H atoms), while only 3.88 moles of H atoms are chemically stored (3 H moles in one AH mole, and 0.88 H moles in 0.22 urea moles), (3.88) / (4.32) = 90%. [f] For the AN : ammonium hydroxide (AH) ratio of 1 : 2/3, 8/3 moles of ammonia are required (equivalent to 8 moles of H atoms), while only 6 moles of H atoms are chemically stored (4 H moles in one AN mole, and 3 H moles in 2/3 AH moles), (6) / (8) = 75%. [g] For the AN : urea ratio of 1 : 1/3, 8/3 moles of ammonia are required (equivalent to 8 moles of H atoms), while only 16/3 moles of H atoms are chemically stored (4 H moles in one AN mole, and 4 H moles in 1/3 urea moles), (16/3) / (8) = 67%.

6. PFP^{flue} indices

The PFP indices for in the case of CO_2 separation from flue gas are given in Table S6.

Table S6. PFP^{flue} indices of the selected alternative fuels

Fuel	separation[a] (GJ ton^{-1})	CO_2 transport[b] (GJ ton^{-1})	PFP index[c]
Methane	2.03	0.318	31%
MeOH	1.02	0.159	32%
DME	1.41	0.222	28%
Ammonia	0.18	–	35%
Aq. AHU	0.22	0.021	28%
Aq. AAN	0.06	–	14%
Aq. UAN	0.14	0.013	13%

[a] Required energy for separating CO_2 from flue gas and N_2 from the atmosphere[13] as feedstock. An estimated required energy for large-scale flue gas CO_2 (e.g., 13.3% vol.) separation of 0.74 GJ ton^{-1} was used.[19,20] [b] Calculated as in Table S3. [c] Calculated according to Equation E3, complimentary data taken from Table S4.

7. Sensitivity analysis

The normalized sensitivity of the PFP index to each parameter is defined as $\left(x / PFP\right) \cdot \left[\partial(PFP) / \partial x\right]$, where x is the respective parameter. Its value indicates the percent change in the PFP index if parameter x changes by 1%. E.g., the PFP^{atm} index of methane would increase by 0.16% if the required energy for atmospheric separation would be reduced by 1%.

Table S7. The normalized sensitivity of the PFP index to its major contributing factors[a]

Fuel	Required energy for atmospheric CO_2 separation[b] (in %)	Required energy for atmospheric N_2 separation[b] (in %)	Required energy for flue gas CO_2 separation[c] (in %)	Required energy for water splitting[b] (in %)	Required energy for fuel synthesis[b] (in %)
Methane	-0.16	–	-0.02	-0.81	-0.01
MeOH	-0.19	–	-0.02	-0.71	-0.10
DME	-0.18	–	-0.02	-0.69	-0.13
Ammonia	–	-0.16	–	-0.94	-0.05
Aq. AHU	-0.07	-0.14	-0.01	-0.84	-0.09
Aq. AAN	–	-0.16	–	-0.92	-0.07
Aq. UAN	-0.06	-0.14	-0.01	-0.84	-0.10

[a] The required energy for the fuel distribution was not included in this analysis since it is by far the least significant factor in the PFP index (Table S4). [b] With respect to PFP^{atm}. [c] With respect to PFP^{flue}.

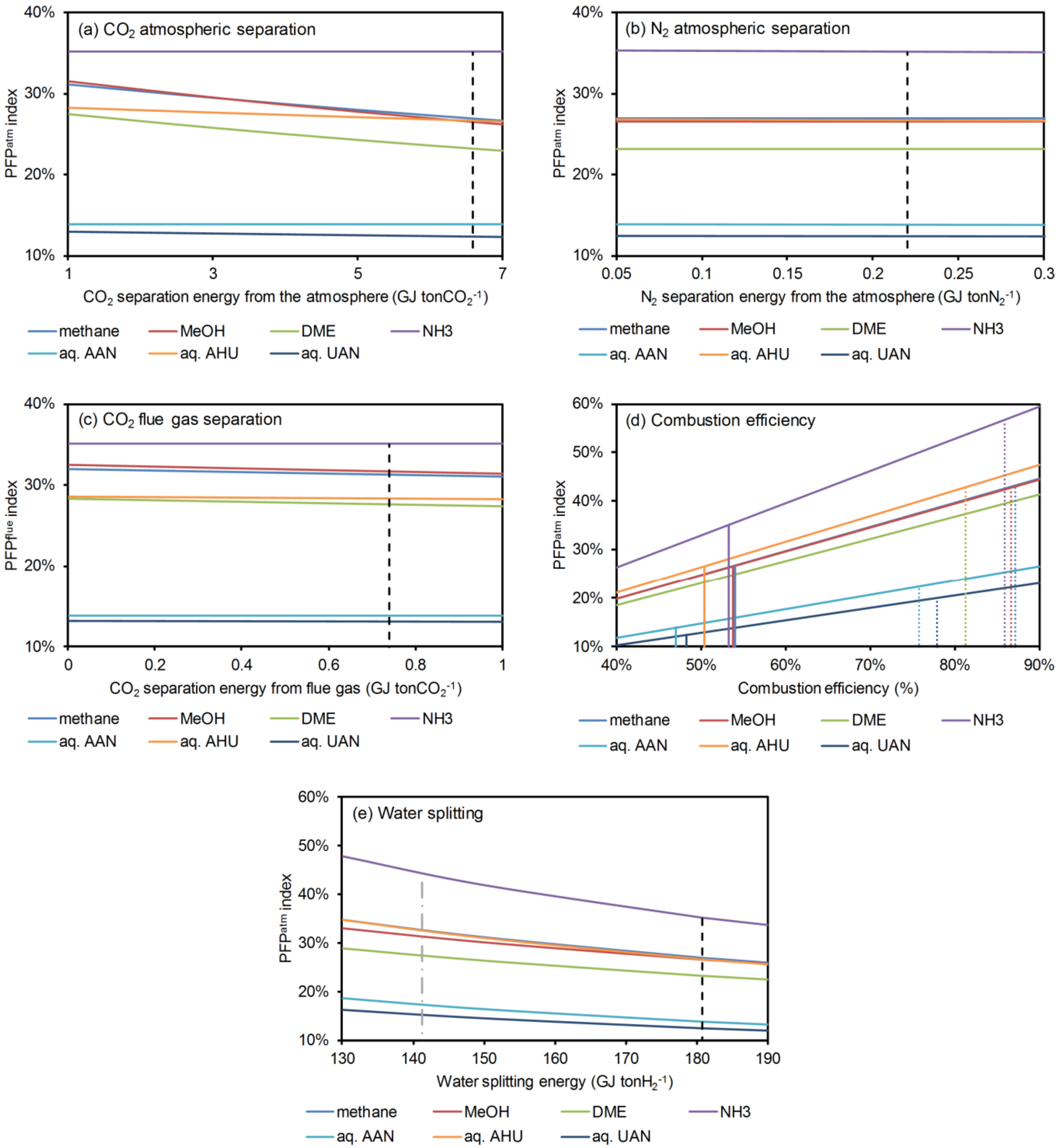

Figure S1. PFP sensitivity analysis. (a-c) Vertical dashed lines represent values used in this work as respectively referenced in the text. (d) The vertical lines are with respect to each individual fuel according to the color legend; solid lines represent current values while the dotted lines represent the Carnot efficiency. (e) The vertical dashed line represents the value used in this work as respectively referenced in the text; the gray dashed and dotted vertical line represents the minimal theoretic required energy for water splitting, 141.8 GJ per ton H_2, which is the standard enthalpy of formation for water in terms of H_2 mass. The curves of methane and aq. AHU nearly align.

8. The required energy for aqueous AAN, AHU, and UAN synthesis

Producing AN from ammonia as a feedstock requires 0.68 GJ ton^{-1} for the ammonia production from H_2 and N_2 in addition to 0.15 GJ ton^{-1} for the synthesis of AN itself.|21| Producing urea requires 0.91 GJ ton^{-1} for ammonia production in addition to 3.3 GJ ton^{-1} urea for the synthesis of urea itself. Finally, the required energy for mixing is estimated at 0.13 GJ ton^{-1}.|21| Therefore, the total required synthesis energy is 0.9 GJ ton^{-1}, 1.8 GJ ton^{-1}, and 1.3 GJ ton^{-1} for aqueous AAN, AHU, and UAN, respectively. Figure S2 presents the flow chart for calculating the required synthesis energy of aqueous UAN as a representative fuel.

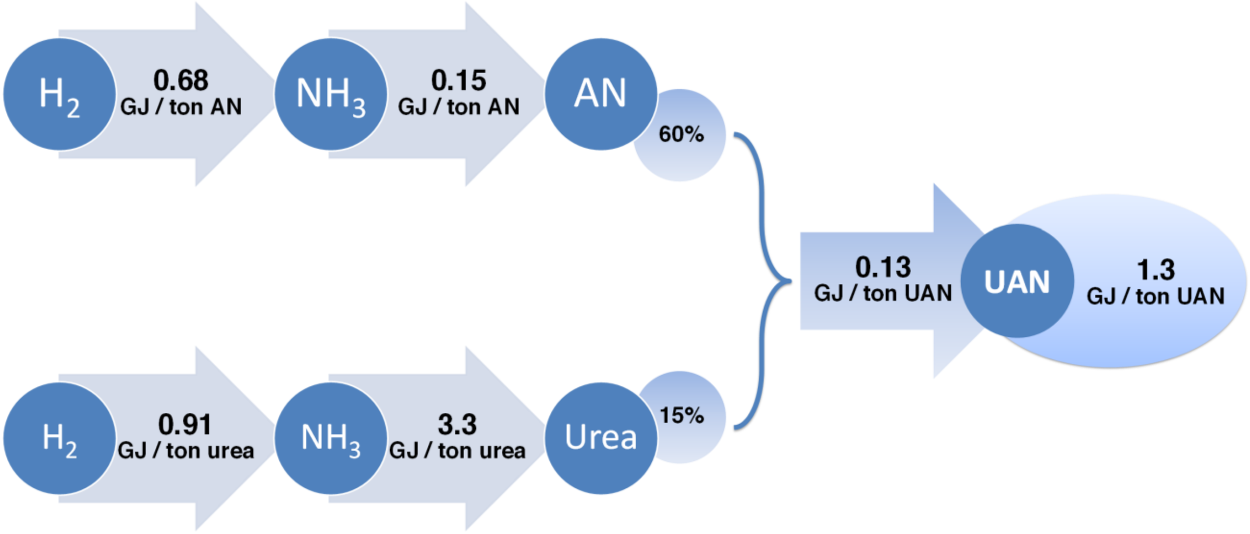

Figure S2. Energy requirement flowchart for the synthesis of aqueous UAN.

9. The required energy for DME synthesis

Dimethyl ether (DME) is produced by methanol dehydration, usually in a fixed bed reactor. The methanol feed is pumped to 20 bar before reacting, and the product DME is then separated from water and non-reacted methanol in a distillation column|21|. The electrical energy required to pump the liquid methanol inlet stream is negligible. Assuming full heat recovery, the energy required for DME synthesis from methanol is 6.6 GJ per ton DME for the MeOH feedstock and 2.016 GJ of thermal energy per ton DME for the synthesis process.|22| According to Equation SE1, the total required energy for DME synthesis is therefore ~8.7 GJ per ton.

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