Electronic supporting information for:

CO from CO_2 and fluctuating renewable energy via formic-acid derivatives

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The sections of the electronic supporting information (ESI) follow in the order that the ESI is mentioned in the in the main paper. The order of the sections is as follows:

- 1. Details exergy calculations
- 2. Details quantum mechanical calculations
- 3. Details of the process flowsheets
- 4. Details of the hierarchical design approach
- 5. The 110 systems for calculation of the exergy loss based on experiments
- 6. Systems evaluated in the hierarchical design approach
- 7. Comparison between experimentally based and predicted exergy (level 2) loss
- 8. List of systems evaluated at level 2
- 9. Special comments regarding formic acid and DIPF
- 10. Reverse water gas shift (RWGS) process

1. Details exergy loss calculations ¹

The total exergy loss is defined as the difference in the exergy streams entering and leaving: $E_{\text{loss}} = E_{\text{in}} - E_{\text{out}} = \sum_{\text{in}} (E_{\text{Q}} + E_{\text{H}} + E_{\text{W}}) + \sum_{\text{out}} (E_{\text{Q}} + E_{\text{H}} + E_{\text{W}})$

Where E_{in} and E_{out} are the exergy of all the streams entering and leaving the SSR process, respectively. These streams include heat (E_Q), mass (enthalpy, E_H) and work (E_W). Furthermore, the surroundings are defined as $T_s = 298.15$ K, $P_s = 1$ bar and with a concentration of 50 % of H₂ and 50 % CO₂ corresponding to the stoichiometric feed.

Exergy of a heat stream where the thermodynamic middle temperature $T_{\rm m} > T_{\rm s}$:

$$E_{\rm Q} = Q \left(1 - \frac{T_{\rm s}}{T_{\rm m}} \right).$$

To obtain the exergy of a heat stream (E_Q) where $T_m < T_s$, we obtain the necessary electricity (P_t) for cooling, by considering a reversible counter clockwise Carnot process. Electricity is pure exergy:

$$E_{\rm Q} = P_{\rm t}.$$

 P_{t} is obtained by dividing the heat (*Q*)that must be removed via cooling, by the coefficient of performance (ε):

$$P_{\rm t} = \frac{Q}{\varepsilon}.$$

Epsilon is found from the temperatures involved:

$$\varepsilon = \frac{T_{\rm s}}{T - T_{\rm s}}.$$

Exergy of a Work stream: Work is also pure exergy:

$$E_{\rm W} = W.$$

Exergy of a mass (enthalpy) stream: The exergy of an enthalpy stream is found from the following:

$$E_{\rm h} = n\{(h - h_{\rm s}) - T_{\rm s}(s - s_{\rm s})\},\$$

where n is the mol flow in mol/s.

2. Details quantum mechanical-calculations

Due to large deviations in experimentally measured and missing Gibbs free energies of reaction (tab. S1), we calculate the Gibbs free energy of reaction by quantum mechanics (QM). Finally, we compare to experimental reaction yields if available; then we choose if we use experimental or QM calculated Gibbs free energy of reaction for each storage molecule.

Quantum mechanical calculations:

The Gibbs free energy of the reaction was calculated with QM using the following equation:

 $\Delta G_{\rm R}^0(T, p^0) = \sum_i \vartheta_i \left(\Delta_{\rm R} E_i^{\rm lim, SPE}(T = 0 \text{ K}, p^0) + E_{\rm Temperature \, correction, i}(T, p^0) + \sum_k \vartheta_k E_{{\rm HR}, k}(T, p^0) \right),$

where "i" represents each species in the reaction, ϑ_i is the stoichiometric coefficient, $\Delta_R E_i^{\lim,SPE}$ is the single point energy at the basis set limit, $E_{\text{Temperature correction},i}$ the temperature correction to the single point energy and $\sum_k \vartheta_k E_{\text{HR},k}$ the hindered rotation correction. Here "k" runs over all relevant hindered rotations in each molecule. ϑ_k is the number of times each hindered rotation k is present in a molecule and $E_{\text{HR},k}$ is the contribution of each hindered rotation "k" to the Gibbs free energy.

The single point energy, temperature correction and hindered rotations are based on the optimized geometry which was obtained with B3LYP/TZVP in Gaussian². All optimized geometries can be found in "Optimized_geometries.zip". Furthermore, the temperature correction calculations were performed with B3LYP/TZVP on the optimized geometries. Finally the hindered rotation of all bonds was performed using TAM*kin*³ after scans of the bond were performed with Gaussian.

The single point energy at the basis set limit ($\Delta_R E_i^{\lim,SPE}$) was found in the following way: Two single point calculations were performed, one with ccsd(t)/aug-cc-pvTZ and one with ccsd(t)/aug-cc-pvQZ using the RI approximation and Turbomole⁴. We extrapolate to the basis set limit using the method from Bak et al⁵, to obtain the most accurate single point energy. The high computational cost of performing ccsd(t)/aug-cc-pvQZ calculations means that it was not feasible to perform single point ccsd(t)/aug-cc-pvQZ calculations for larger molecules such as N,N-diisopropyformamide (DIPF), N,Ndiisopropylamine, N,N-diethylformamide (DEF) and N,N-diethylamine. We obtained the single point energy of these species at the basis set limit by using the method from Klopper et al.⁶. Here, we compare the change in single point energy for the DMF synthesis reaction at ccsd(t)/aug-cc-pvTZ level and at basis set limit ($\Delta\Delta_{R,TZ-to-lim}E_{DMF}^{SPE}$):

$$\Delta \Delta_{\rm R,TZ-to-lim} E_{\rm DMF}^{\rm SPE} = \Delta_{\rm R} E_{\rm DMF}^{\rm inf,SPE} - \Delta_{\rm R} E_{\rm DMF}^{\rm TZ,SPE}.$$

Where $\Delta_{\rm R} E_{\rm DMF}^{\rm TZ,SPE} = \sum \vartheta_i E_i^{\rm aug-cc-pVTZ,SPE}$. The difference $\Delta \Delta_{\rm R,TZ-to-lim} E_{\rm DMF}^{\rm SPE}$ is then used to extrapolate the result from ccsd(t)/ aug-cc-pvTZ for DEF and DIPF:

$$\Delta_{\rm R} E_{\rm DEF}^{\rm lim,SPE} = \Delta \Delta_{\rm R,TZ-to-lim} E_{\rm DMF}^{\rm SPE} + \Delta_{\rm R} E_{\rm DEF}^{\rm TZ,SPE}.$$
$$\Delta_{\rm R} E_{\rm DIPF}^{\rm lim,SPE} = \Delta \Delta_{\rm R,TZ-to-lim} E_{\rm DMF}^{\rm SPE} + \Delta_{\rm R} E_{\rm DIPF}^{\rm TZ,SPE}.$$

Selection of free energy used:

After we obtained the Gibbs energy of reaction from QM, we compare to experimentally measured Gibbs energy of reaction⁷, to decide which value we use in the work (tab. S1).

Storage	Storage molecule synthesis		Value used for calculation	
molecule	$\Delta G_{\rm QM}^{0} \left[{\rm kJ} / {\rm mol} \right]$	$\Delta G_{\rm Exp}^{0} \left[{\rm kJ} / {\rm mol} \right]^{7}$	$\Delta G^{0} \left[{^{kJ}} /_{mol} \right]$	Explanation
MeF	24.9	21.9-64.3 ^a	24.9	Kuhnert et al ⁸ models the reactive
				VLE at low T and P, with $\Delta G_{\rm Exp}^0 =$
				$26.78 - 28.84 \text{ kJ/}_{mol}$, which is
				similar to our QM result. Thus, we
				use our QM result.
EtF	26.3	13.8-60.7 ^ª	26.3	No equilibrium yield was found
DMF	4.44	8.96-15.3 ^ª	9.91 ^c	$\Delta G_{ m QM}^0$ predicts the temperature
				required for CO-reforming at
				significantly higher temperatures
				than reported by Supronowicz et al ⁹ .
				Thus, we use the experimental free
				energy $\Delta G_{\rm Exp}^0 = 9.91 {\rm kJ/mol}$ with
				which we can reach the CO-
				reforming temperature, as reported
				in Supronowich et al ⁹ . Here we use
				heat capacity from QM.
DEF	5.11	Not available	5.11	No $\Delta G_{\mathrm{Exp}}^{0}$ was found.
DIPF	20.9	Not available	20.9	No $\Delta G^0_{\mathrm{Exp}}$ was found.
НСООН	41.4	42.3-44.4	41.4	We use QM result as the range of
				experimental value is small and close
				to the QM result.

Table S1: Comparison to literature.

a) No experimentally measured entropy of formation found for MeF, EtF and DMF, thus we use the QM entropy of formation. Validation for the QM entropy of formation is shown in table S2. c) Using the most recent Gibbs energy of formation values at NIST⁷.

Table S2: Comparison of entropy of formation from quantum mechanics (QM) to experimental values from the literature.

Molecule	$S_{f,QM}^{0} \left[J_{molK} \right]$	$S_{\rm f,exp}^0 \left[\frac{J}{molK} \right]^7$
H ₂	130	130
CO ₂	214	213
СО	197	198
НСООН	248	248-249
MeOH	241	237-249
H ₂ O	189	189
EtOH	282	278-298
DMA	275	268

3. Details of the process flowsheets

This section explains the four possible process flowsheets. Each process flowsheet has five unit operations (fig. S1): (1) storage molecule synthesis, (2) extraction of the storage molecule, (3) purification of the extraction phase (before or after CO-reforming), (4) CO-reforming of the storage molecule and (5) purification of CO (fig. S1).



Additional reactant recycle

Figure S1: Overview of the 5 operations in the SSR process.





Figure S2: process flowsheet SBPB.

1. Storage molecule synthesis (fig. S2)

The storage molecule synthesis is performed in the synthesis reactor. The pressure in the synthesis reactor is adjusted until 95 mol % H_2 conversion is achieved, or a maximum pressure of 200 bar is reached. The CO₂ to H_2 ratio is 1/1. The amount of additional reactant is added stochiometrically to H_2 . If the storage molecule is a formate, the reaction is carried out at the ambient temperature, as this is thermodynamically favored. If the storage molecule is a formamide the reaction temperature is 323.15 K, as elevated temperature favors the formamide over the amine-salt-adduct¹⁰.

In this process flowsheet, the solvent is added in the synthesis reactor. Thus, in in the synthesis reactor, a vapor-liquid-liquid equilibrium (VLLE) is formed. The two liquid phases formed are the extraction and catalyst phase. The added solvent can be either the extraction or the catalyst solvent. This decision is made depending on the partition coefficient of the storage molecule

Extraction phase

 $\frac{x_{storage molecule}}{Catalyst phase}$) at infinite dilution of the storage molecule, in the binary LLE of (P_{storage molecule} = Catalyst phase Xstorage molecule

the solvent and water. If the storage molecule partition coefficient is larger than 1, the added solvent acts as the extraction solvent and otherwise the added solvent is the catalyst solvent.

2. Extraction of storage molecule

In the process flowsheet SBPB, the extraction is performed with a single stage LLE-decanter, as the two liquid phases already are present in the synthesis reactor. The separation of the two liquid phases is performed at reaction pressure and temperature, as otherwise the presence of the homogeneous catalyst would reverse the storage molecule synthesis.

The extraction specification is 99 mol % of the storage molecule formed is extracted into the extraction phase. This specification is reached by adjusting the amount of solvent. Addition of extraction solvent can lead to the disappearance of the catalyst phase when the total composition is outside the LLE-binodal. Thus, we add catalyst solvent until two liquid phases exist again, to ensure two liquid phases for catalyst retention.

3. Purification of extraction phase before CO-reforming

In the SBPB process flowsheet, the extraction phase is purified before the CO-reforming. This is done with distillation. The sequence of distillation columns can vary depending on the boiling points of the components involved and their liquid-liquid equilibria. The purification specifications of the storage molecule are 98 mol % recovery and 98 mol % purity. The purification specification of the added solvent is 98 mol % recovery (could be either extraction or catalyst solvent). The purification specification for water is that we remove excess water (excess beyond what is needed to ensure extraction specifications), that is formed in the storage molecule synthesis.

4. CO-reforming of the storage molecule:

The CO-reforming is performed in the gas phase, following the experimental work by Supronowicz et al⁹. Furthermore, the CO-reforming is favored by a low pressure and elevated temperature, and is thus operated 1 bar and elevated temperature. The CO-reforming temperature is adjusted for 95 mol% CO-yield; however for convergence we do not consider residual storage molecule in the downstream purification.

5. Purification of CO:

The purity specification of the final product, CO, is 99 mol % and 99 mol % recovery. After the COreforming, a stream consisting of the additional reactant and CO is present. The required CO purity is achieved by usage of flashes (VLE), where the CO is removed in the gas phase and the additional reactant is removed in the liquid phase. The temperature of the first flash is operated at a temperature that ensures 99 mol % recovery of CO. Furthermore, if the CO purity in the gas phase from the first flash does not fulfill the 99 mol % purity specification, then the gas phase from the first flash is removed, and sent to a second flash which is operated at a lower temperature. The temperature of this second flash is set so that the 99 mol% CO purity is achieved.

Process flowsheet SBPA (fig. S3):



Additional reactant recycle

Figure S3: Process flowsheet SBPA.

1. Conditions in the synthesis reactor: Same as process flowsheet SBPB

2. Extraction of storage molecule: Same as process flowsheet SBPB

3. Purification of extraction phase after CO-reforming: In the process flowsheet SBPA, the purification is performed after the storage/CO-reforming. The components in the mixture to be purified are the extraction solvent, some catalyst solvent and the additional reactant (storage molecule has been reformed to CO), and could thus be directly recycled to the synthesis reactor. However, it is desired to remove excess water (could be either extraction- or catalyst solvent). This excess water removal can be performed with extraction if the mixture of the extraction solvent, some catalyst solvent and the additional reactant splits into two liquid phases. If liquid-liquid phase separation occurs, we then recover the residual additional reactant from the aqueous liquid phase by distillation. Otherwise as we want to avoid distillation here, we recycle this mixture to the synthesis reactor. Then the excess water must be removed via the purge of the catalyst phase. The purity specifications are the same as for the process flowsheet SBPB.

4. CO-reforming of the storage molecule: Same as in the process flowsheet SBPB, except that now a mixture is present which must be evaporated for the gas phase CO-reforming.

5. Purification of CO: Same as for the process flowsheet SBPB, except that now the flashes are VLLE.

Process flowsheet SAPB (fig. S4):



Additional reactant recycle

Figure S4: Process flowsheet SAPB.

1. Conditions in the synthesis reactor: In the process flowsheets SAPB no LLE is present in the synthesis reactor, as now the solvent is added after the synthesis reactor in the extraction column. This means that the synthesis occurs in water (water is a byproduct of the storage molecule

synthesis), and thus water is the catalyst phase. Any further specifications regarding the storage molecule yield are still the same as in SBPB/SBPA.

2. Extraction of storage molecule: The extraction is performed in an extraction column. Thus, the added solvent can only be the extraction solvent. We add extraction solvent until 99 % of the storage molecule is extracted. Again water addition might be necessary, to ensure that two liquid phases are present in the extraction column. The extraction column is operated at synthesis reactor conditions.

3. Purification of extraction phase before CO-reforming: Same as in process flowsheet SBPB.

4. CO-reforming of the storage molecule: Same as in process flowsheet SBPB.

5. Purification of CO to specifications: Same as in process flowsheet SBPB.

Process flowsheet SAPA (fig. S5):



Additional reactant recycle

Figure S5: Process flowsheet SAPA.

1. Conditions in the synthesis: Same as in process flowsheet SAPB

2. Extraction of storage molecule: Same as in process flowsheet SAPB

3. Purification of extraction phase before CO-reforming: Same as in process flowsheet SBPA.

4. CO-reforming of the storage molecule: Same as in process flowsheet SBPA.

5. Purification of CO to specifications: Same as in process flowsheet SBPA.

Process flowsheets without an additional solvent:

Finally we discuss the process flowsheet of systems where no solvent is added. In these systems the separation of the storage molecule and the homogeneous catalyst are achieved without the addition of an extra solvent.

LLE between storage molecule and water

When a LLE is present between the storage molecule and water, it is not necessary to add another solvent, because two liquid phases for catalyst retention are assured (second solvent task). COSMO-RS predicts such an LLE between the storage molecule DIPF and water. Furthermore, there also is such an LLE between DIPF's additional reactant N,N-diisopropylamine and water. Thus, we define the following system: storage molecule DIPF, no added solvent and process flowsheet SBPA.

Furthermore, a LLE exist between the storage molecule EtF and water, indicating that for EtF systems without an added solvent also could be possible. However, for EtF we could not achieve a viable process without solvents. The reason is that we were not able to achieve two liquid phases in the synthesis reactor. The inability to form two liquid phases stems from the fact that EtF's additional reactant, ethanol, acts as a solubilizer on the LLE between EtF and water. Thus, it is only possible to reach the two liquid phase area (total composition inside the LLE binodal) by synthesizing EtF. The unfavorable $\Delta G^0_{\text{EtF,synthesis}} = 26,3$ kJ/mol means that we could not achieve a high enough EtF concentration in the synthesis reactor, to ensure a phase split into two liquid phases.

The reason that a process without an added solvents is possible for DIPF, is (1) a lower $\Delta G^0_{\text{DIPF,synthesis}} = 20,9 \text{ kJ/mol}$ and (2) the LLE between water and DIPF's additional reactant N,N-diisopropylamine¹¹. This second LLE means that it is possible to reach the two liquid phase area just by adjusting the ratio of water/N,N-diisopropylamine.

Vapor phase separation of methyl formate

The storage molecule MeF is highly volatile, and thus it is possible to separate MeF from the homogeneous catalyst by evaporating MeF into the vapor phase. Therefore, we can design a process flowsheet, the "Vapor phase separation" process flowsheet (fig. S6) and use this process flowsheet in the system, storage molecule MeF, no additional solvent, and process flowsheet "Vapor phase separation". In this vapor phase separation process flowsheet there are two phases in the synthesis reactor, a vapor phase (consisting of MeF and unreacted CO₂ and H₂) and a liquid phase (consisting of water, methanol, residual MeF and the homogeneous catalyst (fig. S6). After the synthesis reactor, a flash (Flash 1) is operated at synthesis reactor conditions ($T_{SR} = 343.15$ K, $P_{SR} = 50$ bar), which separates the liquid phase from the gas phase; here the homogeneous catalyst is retained in the liquid phase. Later, the MeF containing vapor phase is flashed at lower temperature and pressure $(T_{\rm F} = 298,15$ K and $P_{\rm F} = 1$ bar) in a second flash (Flash 2); here the storage molecule MeF is recovered before unreacted CO_2 and H_2 are recycled to the synthesis reactor. The system storage molecule MeF, no additional solvent, process flowsheet vapor phase separation, is not as efficient as the other solvent free system, storage molecule DIPF, no additional solvent and process flowsheet SBPA. This is the case, because the conditions for a favorable flash 1 (high T, low P) are directly opposed to favorable conditions of the synthesis reactor (low T, high P). Thus, we select an optimized tradeoff ($T_{SR} = 343.15$ K, $P_{SR} = 50$ bar). The final exergy loss of the system, storage molecule MeF, no additional solvent and process flowsheet "vapor phase separation" can be found in "ESIsystems.xlsx".



Methanol recycle

Figure S6: Flowsheet of the solvent free process where MeF is separated from the catalyst via the gas phase.

4. Details of the hierarchical design approach

In this section we first discuss the levels of the hierarchical design approach (HDA) in detail, with regard to process models used and property data needed. Afterwards the detailed application of the HDA is discussed.

Levels: As previously mentioned there are two levels in the HDA. In the following the level descriptions are found, split up according to the parts of the process flowsheet: (1) storage molecule synthesis, (2) extraction of the storage molecule, (3) purification of the extraction phase (before or after CO-reforming), (4) CO-reforming of the storage molecule and (5) purification of CO.

Level 1: The first level uses shortcuts to get a coarse estimation of the exergy loss.

1. Storage molecule synthesis: we solve the equation for the reaction equilibrium:

$$\prod_i (x_i \gamma_i p_i^s)^{v_i} = e^{-\Delta G_R^0/_{RT}}$$

where the index "i" runs over all species involved in the reaction. Furthermore if multiple liquid phases are present in the reactor, the liquid-liquid-equilibrium criterion must also be fulfilled:

$$x_i^{\text{Extraction phase}} / \frac{x_i^{\text{Catalyst phase}}}{x_i^{\text{Catalyst phase}}} = P_i^{\infty},$$

where and P_i^{∞} the partition coefficient at infinite dilution in the binary LLE of water and the added solvent. Finally the gas phase was considered to be infinitely large, i.e. at all times are the maximum amount of the CO₂ and H₂ are dissolved in the two liquid phases at all times. This maximum gas solubility was calculated by Henry coefficients.

$$H_{i,j} = \frac{y_i P}{x_i}.$$

2. Extraction of the storage molecule: The extraction of the storage molecule was calculated using constant partition coefficients (P_i^{∞}) for all species "i". If the extraction was performed in a decanter we furthermore use component mass balances over the entire decanter for all species:

$$n_i^{\text{Feed}} = n_i^{\text{Extraction phase}} + n_i^{\text{Catalyst phase}}$$

Where n_i is the mol flow of component "i". Alternatively, when an extraction column is used, the mass balance spans all stages. In particular, we use three stages:

$$n_i^{\text{Extraction phase},k} + n_i^{\text{Catalyst phase},k} = n_i^{\text{Extraction phase},k+1} + n_i^{\text{Catalyst phase},k-1}$$

where "k" represents the stage number.

3. Purification of the extraction phase (before or after storage/CO-reforming): We use both extraction (single stage decanter) and distillation for this purification. If we use extraction, it is calculated in the same manner as described before. If distillation is used, we obtain the heating and cooling demand by using the Underwood equation¹². Furthermore, we split the multicomponent distillation up into binary mixtures, for which the individual heating and cooling demands are calculated, due to convergence issues when >50.000 distillation columns are simulated. For example,

if we want to use distillation to purify a mixture containing the storage molecule, water and solvent (where $T_{\text{boil}}^{\text{storage molecule}} > T_{\text{boil}}^{\text{solvent}} > T_{\text{boil}}^{\text{water}}$), we use one distillation column where the bottom product is the storage molecule, and the top product is a mixture of water and solvent. The top mixture can be separated with a LLE decanter. We obtain the heating and cooling demand of the distillation column by simulating two distillations: 1: storage molecule – water and 2: storage molecule – solvent. The necessary relative volatility for the underwood is calculated for each binary distillation column with the following equations:

$$\alpha_{ij}^{\text{Column}} = \sqrt{\alpha_{ij}^{\text{Reboiler}} \alpha_{ij}^{\text{Condenser}}},$$

where the individual relative volatilities are calculated in the following way:

$$\alpha_{ij} = \frac{\gamma_i p_i^s}{\gamma_j p_j^s}.$$

4. CO-reforming of the storage molecule: The CO-reforming equilibrium is calculated with the following equation:

$$\prod_i (y_i p_{\rm t})^{v_i} = e^{-\Delta G_{\rm R}^0/_{RT}}$$

where y_i is the molefraction of component "i" in the gasphase and p_t is the total pressure, which is 1 bar.

5. Purification of CO: Flash units which are used to purify the CO are calculated with mass balances

$$n_i^{\text{Feed}} = n_i^{\text{Gas}} + n_i^{\text{Liquid}},$$

and the Henry coefficients.

Necessary property data at level 1:

Necessary pure component property data: For enthalpy of vaporization of the solvent, we use Trouton's rule ¹³:

$$\Delta H_{\rm vap} = \frac{88 \text{ J/molK}}{T_{\rm boil}}/T_{\rm boil}$$

where the boiling point is predicted with COSMO-RS. Furthermore, the vapor pressure is also predicted with COSMO-RS. We assume that the heating and cooling beyond evaporation is negligible. Necessary mixture property data: At level 1 all mixture property data which are based on the activity coefficient are predicted with COSMO-RS: relative volatility, partition coefficient and Henry coefficient.

Level 2: The second level uses rigorous process models implemented in Aspen Plus V 8.4 to obtain a more accurate predicted exergy loss.

1. Storage molecule synthesis: we solve the equation for the reaction equilibrium with the process model "CSTR", where a finite gas phase is used. We ensure convergence of our automated

simulations by adding more catalyst solvent than the minimum amount necessary to achieve two liquid phases. Reducing this amount to the minimum would reduce the exergy loss marginally.

2. Extraction of the storage molecule: For the single stage extraction we use the decanter process model, and for the extraction column we use the "extraction column" process model.

3. Purification of the extraction phase (before or after CO-reforming): For all extractions we use the same models as in "Extraction of the storage molecule", and for the distillation we use the rigorous multiphase (VLLE) distillation model "RADFRAC". Convergence of automated RADFRAC simulations can be problematic. We overcome this by employing initial guesses for reflux ratio and distillate to feed ratio from the shortcut model "DSTWU".

4. CO-reforming of the storage molecule: The CO-reforming is calculated with the reactor "RSTOIC" and a 95 % yield at the correct temperature of each storage molecule.

5. Purification of CO: The flashes which are used to purify CO are calculated the process models "Flash-1 (VLE)" and "Flash-2 (VLLE)".

Necessary property data at level 2:

All required pure component property data are taken from the available database "PURE84" in Aspen Plus V 8.4. Mixture property data: To transfer the activity coefficient predictions from COSMO-RS to Aspen Plus, we fitted the COSMO-RS activity coefficient into the NRTL activity coefficient equation. For some systems this was not possible, and thus they were discarded (Details see Excelsheet "ESI-systems.xlsx"). Furthermore, the Henry coefficient that is predicted with COSMO-RS is also regressed into the appropriate Aspen Plus Henry coefficient temperature polynomial.

Details on the applied procedure of the hierarchical design approach:

In the following we explain the detailed procedure of the hierarchical design approach (HDA). The goal of the HDA is to identify a set of systems with the lowest exergy loss at level 2, without simulating all systems on level 2. The size of this set (e.g. the number of systems) has a large influence on the computational cost of the HDA. Thus, we balance the computational cost with size of the set, by defining that we aim to identify the 150 systems with the lowest exergy loss at level 2.

The procedure of the HDA is as follows (fig. S7): We first evaluated all systems at the coarser level 1 (step 1, fig. S7), to obtain the level 1 exergy loss ($E_{1,j}$) of each system "j". We use $E_{1,j}$ to estimate the level 2 exergy loss ($E_{2,j}^{est}$), by using an error bound between level 1 and 2:

 $E_{2,i}^{est} = E_{1,j} \pm Error$ bound. (eq. S1)

 $E_{2,j}^{est}$ can then be used to identify the systems, potentially among the 150 most efficient at level 2. This identification is dependent on the error bound: The error bound describes the deviation in exergy loss between levels 1 and 2 ($E_{1,j} - E_{2,j}$), and is obtained by calculating a 90 % confidence interval of the exergy loss deviation ($E_{1,j} - E_{2,j}$), from all systems where both $E_{1,j}$ and $E_{2,j}$ are known. Thus, obtaining an error bound means performing



Figure S7: Flowsheet of the HDA.

computationally expensive level 2 simulations; simulating a large number of systems on level 2 increases the accuracy of the error bound, but also the computational expense. Here, we balance computational expense and accuracy, by using representative systems. The representative systems are simulated on level 2 (step 2, fig. S7), so that we can obtain an initial error bound (step 3, S7). We ensure that the initial error bound is representative by including all storage molecules, important

solvents classes (alcohols, ketones, aldehydes, etc.) and all process flowsheets in the set of representative systems (The list of representative systems can be found in "ESI_CO2toCO.xlsx"). Later during the HDA, when we have simulated more systems than the representative at level 2, will update the initial error bound (step 8, fig. S7). The final error bound can be seen in figure S8.

The next task is to use the estimated level 2 exergy loss ($E_{2,j}^{est}$, eq. S1) to identify the systems that potentially are among the 150 most efficient at level 2 (Step 5, fig. S7). We perform this identification by comparing $E_{2,j}^{est}$ to the exergy loss of the 150th most efficient system at level 2 (150 lowest $E_{2,j}$), that we currently have identified (E_2^{150th}):

$$E_2^{150\text{th}} > E_{2,j}^{\text{est}}$$
. (eq. S2)

If $E_{2,j}^{\text{est}}$ is below $E_2^{150\text{th}}$ then system "j" could be among the 150 most efficient and must be evaluated on level 2.

The next step is the convergence criteria of the HDA (step 6, fig. S7): Check whether all systems fulfilling eq. S2 have been evaluated on level 2. If they have not, these systems must be evaluated on level 2 (step 7, fig. S7). During these evaluations, we continuously update the error bound and E_2^{150th} (step 8, fig. S7). Thus, the HDA is an iterative method. The iteration is continued until the all systems fulfilling eq. S2 have been evaluated at level 2 (step 6, fig. S7). Then we have identified the 150 most efficient systems at level 2. However, it should be noted that more efficient systems could exist.

Figure S8: The distribution of $E_{1,j} - E_{2,j}$ for all >1800 systems "j" that were evaluated on both levels 1 and 2, together with the 90 % confidence interval (red area under graph). The deviation $E_{1,j} - E_{2,j}$ is not normal distributed. Thus, we obtain the 90% confidence interval by selecting the median of the deviation $E_{1,j} - E_{2,j}$ and counting 90% of all systems in each direction from the median. The median is -4.22 kJ/mol CO, while the 90 % confidence interval spans from -188.12

kJ/mol CO to 1.62 kJ/mol CO. Furthermore, it can be seen that level 1 mostly underestimates level 2. We only show $E_{1,j} - E_{2,j}$ from -50 to 20 kJ/mol CO, to improve readability of the figure.

5. The 110 systems for calculation of the exergy loss based on experiments

We need experimental property data for the experimental verification. These necessary data were found in the Aspen Plus databases, Pure84, NIST84, VLE-Aspen, LLE-Aspen, LLE-Lit, VLE-Lit. The systems can be found in the Excelsheet "ESI-systems.xlsx". Furthermore, we consider the LLE between N,N-diisopropylformamide – water to be experimentally confirmed, because COSMO-RS correctly predicts the LLE between water and –N,N-dibutylformamide¹⁴.

6. "Systems evaluated in the hierarchical design approach

Further systems evaluated with the HDA can be found in the excelsheet "ESI-systems.xlsx".

7. List systems evaluated at level 2

The systems evaluated at level 2 can be found in the excelsheet "ESI-systems.xlsx".

8. Comparison between the exergy loss based on experiments and predicted exergy (level 2) loss

We compare E_{exp} and E_2 for all systems of the experimental subset (fig. S9). In this comparison, E_{exp} is lower than E_2 for almost 50 % of the 110 systems (fig. S9). Thus, it is highly likely that for some of the most efficient systems, the low predicted exergy loss E_2 would be confirmed by the experimentally based exergy loss E_{exp} , if the necessary property data were measured.

Figure S9: Integrated deviation between the level 2 exergy loss (E_2) and the exergy loss based on experiments (E_{exp}). Only 88% of the systems are plotted for readability.

9. Special comments regarding formic acid and DIPF

Formic acid: We do not consider the second role of the solvent (separation of formic acid and homogeneous catalyst through use of a LLE) for formic acid. The reason is that $\Delta G^0_{\text{synthesis}}$ for formic acid is so unfavorable, that unless the storage molecule yield is shifted significantly with solvents, formic acid will not be competitive. A solvent "1" that shifts the formic acid equilibrium significantly could then be either the extraction or the catalyst solvent (fig. S11).

Figure S11: Schematic formic acid extraction from the catalyst to the extraction solvent.

If solvent "1" is the extraction solvent, then adding a second catalyst solvent only dilutes formic acid from the extraction phase. Thus, adding a catalyst solvent to the reactor only increases the exergy loss. On the other hand solvent 1 is the catalyst solvent; then we would need a second extraction solvent, solvent "2". Solvent 2 then needs even stronger interactions with formic acid, so that formic

acid is extracted from this catalyst solvent (solvent 1). The second extraction solvent (Solvent 2) would determine the formic acid synthesis equilibrium yield, and by extension the exergy loss of this system; now the exergy loss would be higher than if the solvent 2 was employed alone. The evaluation of solvent 2 alone is also performed in this work. Thus, the comparison of formic acid to the other storage molecules, as done in this work, favors formic acid.

DIPF: We have considered DIPF even though its synthesis from CO₂, H₂ and N,N-diisopropylamine has only been shown indirectly; the synthesis of the intermediate N,N-diisopropylamine-formic acid adduct was shown by Blas Molinos.¹⁵ This intermediate can be converted to the formamide, as has been shown for the formamides DMF and DEF. However, Blas Molinos reported that such a reaction did not take place. In our opinion this does not disqualify DIPF as a storage molecule as still a change of reaction conditions or catalyst could enable the DIPF synthesis. The possibility of the DIPF synthesis from CO₂, H₂ and N,N-diisopropylamine is made plausible as other researchers have used stronger reduction agents than H₂, such as silanes,¹⁶ to produce DIPF from CO₂ and N,N-diisopropylamine. Thus, we still consider DIPF as a storage molecule since DIPF has favorable LLEs with water. The necessary pure component parameters for DIPF are taken from literature.¹⁷

10. Reverse water gas shift (RWGS) process

Figure S12: The reverse water gas shift process from^{18a}. First the reactants CO_2 and H_2 enter the reverse water gas shift (RWGS) synthesis reactor, where water and CO are formed. In the next step water is removed by condensation, followed by an amine wash and an absorber for CO_2 recovery. Finally a low temperature methane wash separates hydrogen from CO.

In this work we consider two variants of the RWGS process: RWGS (CO2RRECT) is simulated in literature^{18a}, and RWGS (This work) is simulated in this work. Both variants use the flowsheet in figure S12. In the following we elaborate on the simulation of RWGS (this work): In the synthesis reactor the reaction yield is obtained by equilibrium calculations at 1200 K and 1 bar^{18b}. The following condensation is operated at 298.15 K and 1 bar. The energy demand of the amine wash is determined with performance values from Mueller et al^{18c} which states a heating demand of 2 MJ_{th}/t CO₂ captured; supplied to the reboiler of the CO₂-desorbtion column at 393.15 K. We assume no exergy cost of the absorber. The energy demand of the low temperature methane wash is modeled with a performance value of 1.29 kWh electricity/kg H₂ removed^{18d}. The simulations are performed in Aspen Plus v. 8.4 with ideal gas.

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