EXERGETIC ANALYSIS OF THE UTILIZATION OF EXHAUST CO_2 FOR THE CHEMICAL STORAGE OF RENEWABLE ENERGY

Liisa K. Rihko-Struckmann[1*], Andreas Peschel[1], Richard Hanke-Rauschenbach[1] and Kai Sundmacher[1,2]
[1]Max Planck Institute for Dynamics of Complex Technical Systems,
[2]Otto-von-Guericke University Magdeburg, D-39106 Magdeburg, Germany

Summary

The thermodynamic and operational boundaries for the possible reutilization of CO_2 in the chemical storage of fluctuating renewable energy were quantitatively analyzed in the contribution. Methanol was found to be a suitable chemical storage, which could be produced from CO_2 and hydrogen, and therefore the storage route with methanol was investigated in detail. The exergy chain analysis revealed that the exergy losses are severe in all systems including the conversion to chemical storage. Hydrogen seems to have the best efficiency in stationary systems, where its storage problem is easier to overcome than in mobile systems. CO_2 based methanol could be used as fuel for transport due to its relative high energy density and easy storage.

Keywords CO_2 utilization, sustainability, exergetic analysis

Introduction

The sequestration of CO_2 has been regarded as a solution for CO_2 emissions but unfortunately it handles the concentrated CO_2 stream only as a waste to dispose, and the highly complex CO_2 removal does not produce any added value for the power plant but causes only significant additional costs and remarkable efficiency deficit [1].

The utilization of CO_2 as carbon source for chemical synthesis and the production of fuels has got a great deal of attention as it is emphasized that the reuse of exhaust CO_2 could contribute positively to the global climate change. The production of chemicals from CO_2 has a positive but only very small impact on the global carbon balance [2]. The utilization of CO_2 for fuel production could, in turn, make a significantly larger impact as globally fossil sources (mostly mineral oil) are consumed clearly more as fuel for transport than for chemical production.

A chemical storage of solar or wind energy is highly desired, as both renewable energy sources suffer from intermittent and fluctuating character. Hydrogen can be seen as a chemical, gaseous storage as it can be produced sustainably by electrolyzing water with electricity from solar and wind. On the other hand, hydrogen is the key component also in the CO_2 reuse, as CO_2 itself is thermodynamically extreme stable without exergetic value.

Our approach here is to analyze systematically the existing thermodynamic boundaries for the possible reuse of CO_2 in the chemical storage of fluctuating renewable energy. Furthermore, we declare in the contribution the overall exergetic efficiencies of these alternative routes of storing and converting energy.

Evaluated Process Routes

Figure 1 illustrates the main routes where CO_2 could be involved to store energy chemically. Methanol (CH_3OH), dimethyl carbonate (DMC) and dimethyl ether (DME) are suitable candidates not only as stationary storage but also as transport fuel applicable with existing infrastructure and vehicle fleet. On the other way, dry reforming of CH_4 with CO_2 or the *reverse*-water gas shift reaction produce synthesis gas which in turn can be used e.g. in the Fischer-Tropsch synthesis to produce hydrocarbon fuels.

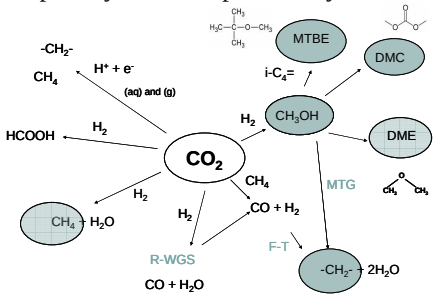

Figure 1. Possible routes for the use of CO_2 to chemical storage of renewable energy.

* To whom all correspondence should be addressed: rihko@mpi-magdeburg.mpg.de, tel: +49-391-6110318

In order to evaluate the energetic and exergetic *overall* efficiency of the energy storage-conversion systems, the thermodynamic limitations of each step were examined in detail. In the present contribution, the route including methanol was compared to hydrogen storage route.

The electric work needed in an electrolyser was calculated with Equation (1)

$$\tilde{w}_{t,12} = \Delta_R \tilde{h}(T) - T \cdot \Delta_R \tilde{s}(T) + \tilde{q}_{12,irr} \qquad (1)$$

where $T \cdot \Delta_R \tilde{s}(T)$ is the reversible heat needed in the reaction. The irreversible part $\tilde{q}_{12,irr}$ includes contributions from the electrochemical anodic, cathodic and ohmic overvoltages $\tilde{q}_{12,irr} = (\eta_{an} + \eta_{cat} + i \cdot R_\Omega) \cdot z \cdot F \cdot$ The electrolyzer overvoltages in our analysis were taken from operational literature values. The exergy based efficiency, η_E, of the electrolyzer calculated as a ratio of the chemical exergy of the produced hydrogen to the supplied electric work was 0.62.

In the methanol synthesis the following reactions (2-4) establish the reaction equilibria:

$CO_2 + 3\ H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H < 0 \quad (2)$
$CO + 2\ H_2 \leftrightarrow CH_3OH \quad \Delta H < 0 \quad (3)$
$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H > 0 \quad (4)$

The process was simulated with recycle stream of the unreacted feed compounds CO, CO_2 and H_2 (see Fig. 2) with four adiabatic reactor units (T_{in} = 220°C) having intermediate cooling, the process pressure 50 bar, nonidealities regarded by SRK equation, Δp=0.25 bar in the reactors and the heat exchangers.

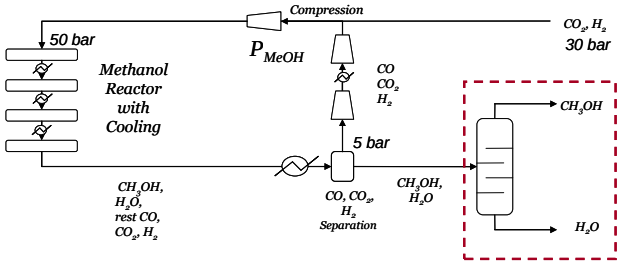

Figure 2. Simulated methanol process.

The recycle ratio n_{feed}/n_{tot} 4.7 guarantees complete conversion. The complete mass and energy balances were obtained from the simulation results, which were used in the overall efficiency analysis. Excess heat is generated due to exothermic reactions, but additional work, P_{MeOH} was needed for the gas compression in the unit, which decreased the overall efficiency. The ratio between P_{MeOH} and the exergy of the product was 0.22.

The last part of the energy conversion system was the conversion of the methanol to electricity, which was calculated applying either a molten carbonate fuel cell (MCFC) or a combined cycle power plant (CCPP) with known operational efficiencies of η_{el} 0.50 % for MCFC and 0.57 % for CCPP, respectively.

Results

Figure 3 gives an overview the whole energy conversion route which was described in detail above.

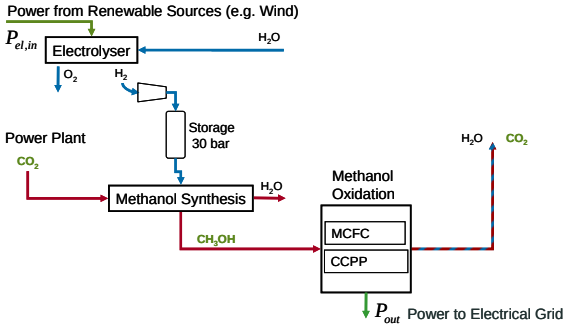

Figure 3. The overall route for the energy conversion analysis.

The exergy chain analysis of the above route is illustrated in Figure 4.

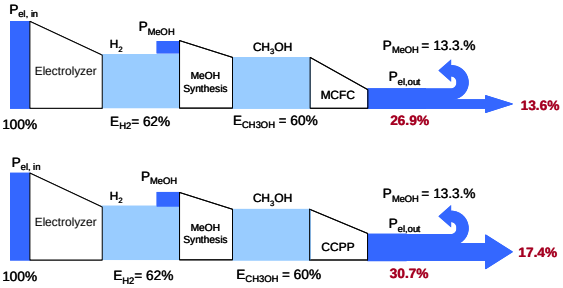

Figure 4. The exergy chain analysis for the methanol route.

As seen in Figure 4, a remaining exergy in the methanol storage route is 13.8 or 17.4 %, respectively, of the initial value. If we compare the results in Fig. 4 to the chain analysis of the hydrogen route (Fig. 5) one can conclude that due to fewer conversion steps the hydrogen route is energetically clearly more attractive. However, if the storage and transport issues are regarded, liquid methanol is more advantageous over hydrogen.

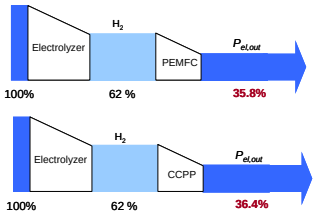

Figure 5
The exergy chain analysis for the hydrogen route.

References

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