# Green Energy Storage: A Developing Technique to Store Excess Electricity with Bicarbonate Salts

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In this work a chemical energy storage facility is designed. Fluctuating energy can be normalized by storing the excess of energy in form of ammonium formate. When demand is high the reverse process can deliver constant electricity. The roundtrip efficiency of this design using existing technologies is 21 %. The capital and operational expenditures are €38 M and €10 M/y to generate 5 MW of constant power from a fluctuating energy source. The breakeven energy price after storage is €0.33/kWh. After future development this system should be capable to compete with alternative storage methods.

## 1. Introduction

Nowadays fossil fuels are used as the main energy source; however, the current fossil fuel sources are running empty and new sources are difficult to find and use. Negative aspect about the use of these sources is the emission of greenhouse gases, which contribute to climate change (Rudin et al. 2017). With these negative aspects of the use of fossil fuels, the demand for renewable sources is growing. In this study, the focus will be renewable energy storage in the Netherlands. The main challenge of using these sources are matching the supply with the demand, due to fluctuations.

Currently, there is not enough green electricity produced. Germany and Denmark did invest in green energy sources on a large scale, therefore they regularly have an excess of energy (Martin 2016). To store such an excess of electricity, batteries could work as a short time storage facility. But for longer periods of time the metals needed will become scarce and therefore it will be an expensive solution. Some alternative storage facilities are: chemical energy storage, compressed air energy storage and pumped hydro. In this report a chemical energy storage facility is proposed as a solution for energy storage. As a chemical storage, the bicarbonate/formate system is selected because it has a high yield and activity (Su et al. 2015). This system is $CO_2$ neutral and the properties of the system were to be investigated
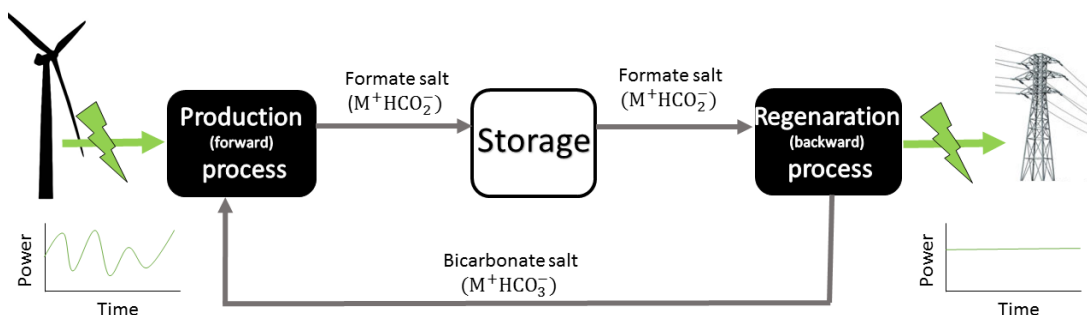


*Figure 1: Proposed chemical energy storage process*

## 2. Chemistry

When hydrogen is stored as an energy carrier, the gas requires high pressures in order to obtain a feasible energy density. It is possible to store hydrogen in the form of an ammonium formate salt by reacting hydrogen with an ammonium bicarbonate. The aqueous formate has a higher energy density then hydrogen gas at atmospheric pressure. Since this is an equilibrium reaction, the formate can be transformed back into hydrogen when desired. The forward reaction is favoured by low temperature and high pressure (40 °C, 27.5 bar), whereas the reverse reaction is favoured by high temperature and low pressure (100 °C, 2.5 bar). The reaction is catalysed by palladium on activated carbon 5 wt% Pd/AC (Su et al. 2015)

$$NH_4HCO_3 + H_2 \Leftrightarrow NH_4HCO_2 + H_2O \tag{1}$$

## 3. Process Design

In this project, it is assumed that a wind park with 25 turbines supplies excess 13.75 MW of electricity. The goal in terms of production capacity is to produce 5 MW of power when there is a demand for it. The first alternative design is to use a direct bicarbonate electrolyser but there is not enough data on this system available yet and therefore this is not chosen. A separate water electrolyser and reactor is chosen. The type of the electrolyser that was chosen is a Polymer Electrolyte Membrane (PEM) with 1.25 MW power capacity. This can handle the fluctuations and has a short start-up time. As the wind power fluctuates, the number of activated PEM electrolysers can be altered between 1 to 11.
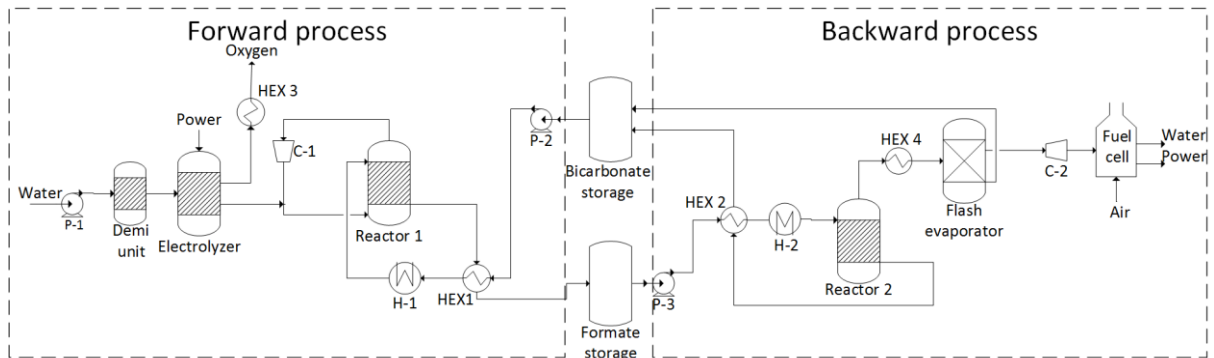


Figure 2: Process design. Left is production process, right is regeneration process. (p = pump, c = compressor, H = heater and HEX = heat exchanger)

The produced hydrogen gas enters into the first reactor which is the hydrogenation reactor. The Pd/AC catalyst can reach yields of almost 100 %. The optimal process conditions for this type of catalyst is 40 ˚C, a pressure of 27.5 bar and a residence time of 3 h, resulting in a formate yield of 80 %. The 2 % bicarbonate left in the solution will be included in the formate storage. A higher temperature will lower the maximum yield that can be obtained. The water to salt (bicarbonate) ratio is 13.5:1(Engel, 1994).  After the first reaction, the mixture of liquid and gas are to be separated via flash column. For the alternative designs, the mixture is depressurized before entering the flash drum. However, difference in operating between high or low pressure does not make a large difference in the heat duty. Therefore, separation at the same pressure of the reactor is preferred. Before entering the storage tank, the water can be partly evaporated to reduce the size of the storage tank. Operating cost of the evaporation of water is high, because there are large amounts of water and water has a high enthalpy of vaporization. Therefore, it is chosen to build a bigger storage tank and not evaporate the water.

The second reactor, a dehydrogenation reactor, is operated at a pressure of 2.5 bar and a temperature of 100 ˚C. Raising the temperature is necessary in order to reach a feasible yield. The resulting $H_2$ gas is separated from the mixture at 2.5 bar by a simple phase separator, which will not consume energy, since the system is already split into two phases. Both are slurry reactors with internal filtration to minimize mass transfer limitations. To generate power from the hydrogen which comes out of the separator, a power production unit is used. A fuel cell is selected in favour of a gas turbine as the fuel cell can cope with fluctuations better and has a higher electrical efficiency.

Other designs are considered as a solution for the fluctuating energy storage. First the type of salt, sodium and potassium are both candidates for storing energy. However, those are not selected because of the lower solubility in water and their lower yield towards formate. Secondly, the use of an alkaline electrolyser. Despite

its lower costs it cannot deal with fluctuations well and it has a longer startup time. Another major alternative is the use of a gas turbine or various types of fuel cells (Solid oxide, Molten Salt, PEM and Phosphoric acid). The choice has been made for the PEM fuel cell because it has a high electrical efficiency (50 – 60 %) and it can deal with fluctuations.

## 4. Technical Evaluation

Due to the fluctuations in the excess wind power, individual electrolysers need to be started up and shut down often. This means the corresponding reactors need to be started up and shut down as well. In case of the forward reaction, a drop-in wind power will lead to a shutdown of electrolysers. A rise in wind power will result in one or more electrolysers being started up. The electrolysers operate at their nominal load of 1.25 MW (Siemens 2015). For a park of 25 wind turbines, eleven electrolysers are necessary. Aspen was used to model the plant so that the heat duties of each equipment (see Table 3) and composition streams can be calculated. From the Aspen simulations, data from the heat duties can be used to calculate round trip efficiency and energy requirements or operating cost. The capitals costs are calculated with Aspen, existing data and correlations from literature. Due to the complexity of the chemistry, the reactors are modelled in Matlab from which the conversion is used in the aspen simulation.

*Table 1: Capital cost of design*

| Equipment Name | Equipment Label | Size | Equipment Cost (€) | Remarks |
|---|---|---|---|---|
| Water-Pump | P-1 | - | - | Included with the Electrolyser costs. |
| Forward Feed-Pump | P-2 | 15.6 kW | 39,000[a] | |
| Backward Feed-Pump | P-3 | 7.6 kW | 5,500[a] | |
| Recycle compressor | C-1 | 5 kW-2,000kW | 10,000[d] | |
| Electrolyser | | 1.25 MW | 2,000,000 [b] | Costs to have an operating electrolyser, includes demineralizer |
| Forward Reactor | R-1 | 1.5 m$^3$ | 42,800[c] | Non-agitated |
| Backward Reactor | R-2 | 0.3 m$^3$ | 13,300[c] | Agitated |
| Fuel Cell | | 5 MW | 265,000[e] | |
| Flash vessel | F-1 | 2.4 m$^3$ | 13,500[a] | |
| Heat exchanger | HEX1 | 7.1m² | 9,600[a] | |
| Heat exchanger | HEX2 | 690 m² | 130,000[a] | |
| Water cooler | HEX4 | 91.7m² | 23,700[a] | |
| Heater | H-1 | | | |
| Steam heater | H-2 | 59.0m² | 17,750[a] | |
| Storage tank | S-1 | D = 27m, H = 15m | 647,355[c] | |
| Storage tank | S-2 | "" | 647,355[c] | |

| | |
|---|---|
| CapEx forward process | €2,101,400 |
| CapEx forward process with Lang Factor | €2,466,440 |
| CapEx backward process | €468,750 |
| CapEx backward process with Lang Factor | €2,156,250 |
| Costs Storage tanks with Lang Factor | €5,955,666 |
| Total Costs with 11 times the Forward Process | €35,242,756 |

*(a) Price indication obtained with Aspen Plus (b) Price indication provided by Siemens (c) Price indication obtained through Matche.com (d)Price indication via Alibaba.com (e) Price indication by the USA Department of Energy* (USA Department of Energy 2015)

The plant has a high CapEx of €35 M because the PEM electrolysers are expensive (€ 2 M/unit). When electrolyser technology becomes more mature, their cost should be reduced significantly. The OpEx (€ 10 M is heavily affected by the CapEx due to depreciation and maintenance costs. Also, about 13 % of the OpEx is spend of refreshing the catalyst. Selling the oxygen produced in the electrolysers contributes to almost €700,000 on yearly basis. The description of the capital cost and the operational costs are given in Table 1 and 2. The calculations are guided by literature (Seader et al., 2008).

11 Electrolysers are operated at their nominal load of 1.25 MW when the wind park is operating at a capacity factor of 50% over the year. Taking 8,400 h/y, this leads to 934,511 kmol of H2 being produced each year. The input required to power the 5 MW fuel cell is 169 kmol/h. Combining these two number leads to the conclusion that the backward reaction is operated for 5,546 h/y. In Table 3, the energy produced and consumed by each unit operations per year can be found. It should be noted that HEX 4 is included in this table and is producing energy, but this energy cannot be used anywhere in the process.

*Table 2. Operating costs of design*

| | Cost factor | Typical factor in SI unit | Cost (€/y) |
|---|---|---|---|
| Feedstocks | | | |
| | Process water | 0.2 $/m$^3$ | 1,780 |
| | Catalyst loading forward | 3.5 $/g | 1,296,046 |
| | Catalyst loading backward | 3.5 $/g | 170,198 |
| Utilities | | | |
| | Electricity | 0.04 $/kWh | 77,765 |
| | Cooling water | 0.013 $/m$^3$ | 14,438 |
| | Low pressure steam | 6.6 $/ton | 131,286 |
| Operations (O) | | | |
| | Direct wages and benefits (DW&B) | 35 $/operator-hr | 523,320 |
| | Direct salaries and benefits | 15 % of DW&B | 78,498 |
| | Operating supplies and services | 6 % of DW&B | 31,399 |
| | Technical assistance to manufacturing | 60,000 $/shift-yr | 267,000 |
| | Control laboratory | 65,000 $/shift-yr | 289,250 |
| Maintenance (M) | | | |
| | Wages and benefits (MW&B) | 4.5 % of $C_{TDC}$ | 1,411,482 |
| | Salaries and benefits | 25 % of MW&B | 352,871 |
| | Materials and services | 100 % of MW&B | 1,411,482 |
| | Maintenance overhead | 5 % of MW&B | 70,574 |
| Operating overhead | | | |
| | General plant overhead | 7.1 % of M&O-SW&B | 167,998 |
| | Mechanical department services | 2.4 % of M&O-SW&B | 56,788 |
| | Employee relations department | 5.9 % of M&O-SW&B | 139,604 |
| | Business services | 7.4 % of M&O-SW&B | 175,097 |
| Property taxes and insurance | | 2 % of depreciable capital | 627,229 |
| | | | |
| Deprecation | | | |
| | Direct plant | 8 % of ($C_{TDC}$ - 1.18 $C_{ALLOC}$) | 2,500,000 |
| | Allocated plant | 6 % of 1.18 $C_{ALLOC}$ | 16,000 |
| Cost of Manufacturing (COM) | | | 9,798,229 |
| | | | |
| General expenses | | | |
| | Selling (or transfer) expense | 3 %(1 %) of sales | 20,131 |
| | Direct research | 4.8 % of sales | 32,210 |
| | Allocated research | 0.5 % of sales | 3,355 |
| | Administrative expense | 2.0 % of sales | 13,421 |
| | Management incentive compensation | 1.2 5% of sales | 8,388 |
| General Expenses (Ge) | | | 77,506 |
| Total Production Cost (C) | | COM+GE | 9,876,734 |
| Total Sales | | | 671,040 |
| Yearly Profit | | | -9,204,689 |

*Table 3. Energy consumed and produced by each unit per year*

| Equipment | units | Duty (kW) | Hr/ | Energy (MWh) |
|---|---|---|---|---|
| Fuel cell | 1 | -5,000 | 5,546 | -27,730 |
| Electrolyzers | 11 | 1,250 | 8,400 | 115,500 |
| Pump 2 | 11 | 15.6 | 8,400 | 1,441 |
| Heater 1 | 11 | 7.2 | 8,400 | 665 |
| Compressor 1 | 11 | 0.15 | 8,400 | 14 |
| Heater 2 | 1 | 2,453 | 5,546 | 13,604 |
| Pump 3 | 1 | 7.6 | 5,546 | 42 |
| HEX 4 | 1 | -365 | 5,546 | -2024 |
| Total produced | | | | 27,730 |
| Total consumed | | | | 131,266 |
| Efficiency | | | | 21.1% |

Figure 3 shows that the system loses most of its energy in the electrolyser and the fuel cell. The rest of the system works quite efficient. The bicarbonate solution that leaves the storage tank at 20 °C is the stream that has the lowest energetic value and is therefore selected as the baseline of 0 MWh/y. All other arrows show how much energy on annual base streams from one unit to another, and at what unit operations the energy is lost. Other notable locations were energy is lost is in the storage tanks. As determined for the heat integration the liquid enters the storage at 30 °C, and leaves at 20 °C. The excess heat cannot be used at another place and is therefore lost.
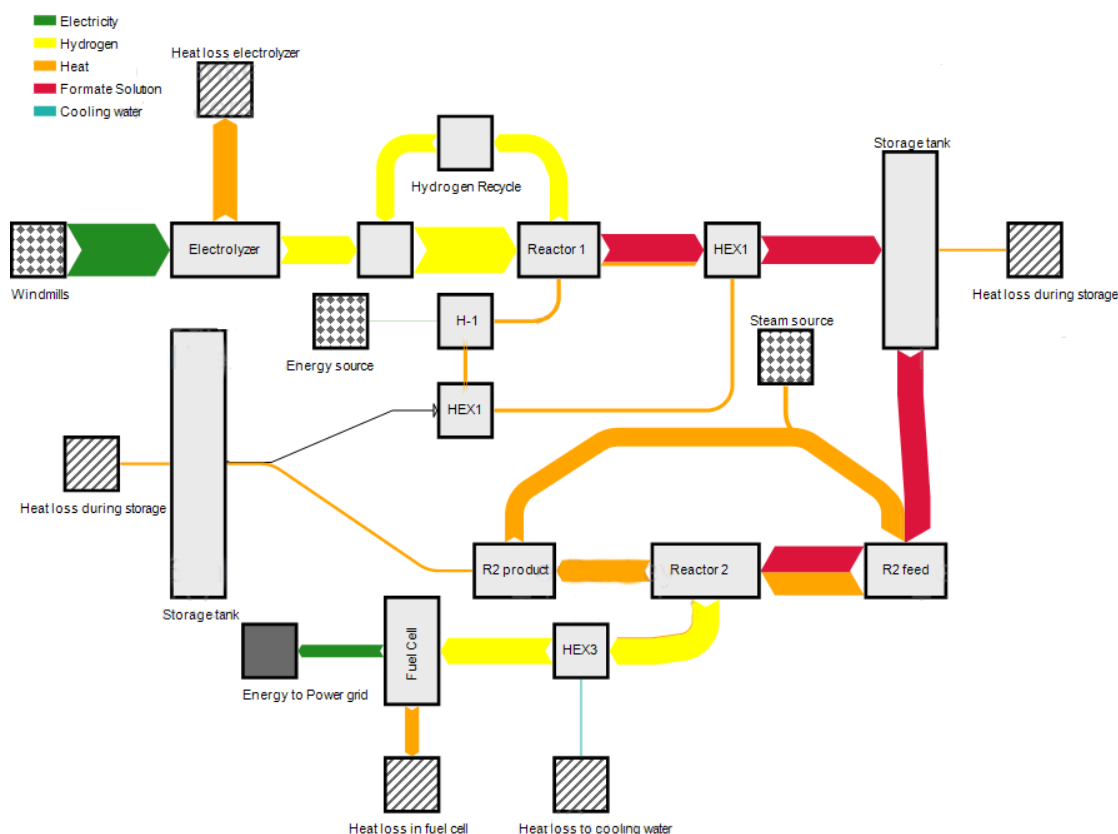
*Figure 3: Sankey diagram of the design*

A safety analysis was performed as well using the fire and explosion index (F&EI) and the chemical and exposure index (C&EI). It was found out that the F&EI for this process is 93. This means the process is considered to be moderately dangerous in terms of fire and explosion risk. It is worth noting that the F&EI is applied for amounts of 454 kg or more. The largest $H_2$ stream in the process is 170 kmol/h, or 340 kg/h This 454 kg of hydrogen will never be present in the same place in this process, so the stream is actually not big enough to apply a F&EI. Second is the CEI, which calculates the harm for humans when exposed. The diameter of the pool size caused by a possible rupture is large, but the chemicals used are not toxic, volatile and corrosive. Leaks can be contained within dikes in order to minimise the pool size. In terms of safety, this process should not pose as a great hazard.

## 5. Process economics and potency

When considering the overall process economics and the power generation of 27,730 MWh/y, it can be concluded that the production price per kWh is €0.33. If the bicarbonate/formate system wants to compete with existing storage techniques, its price should be approximately €0.15 to €0.20/kWh as shown in table 4. By looking at the OpEx, it can be seen that most of the costs are made in the depreciation (25 %) and maintenance (33 %). These numbers are both directly related to the total depreciable capital, which is largely determined by the cost of the electrolysers.

*Table 4. Comparison of energy storage techniques*

| Storage technique | €/kWh |
|---|---|
| Bicarbonate/formate process | 0.33 |
| Pumped hydro | 0.17 – 0.25 (Lazard 2015) |
| Battery (zinc) | 0.21 – 0.34 (Lazard 2015) |
| Compressed air | 0.17 (Lazard 2015) |

Considering the potency of the process the first step would be to increase the salt concentration to the solubility limit (water to salt ratio of 5:1). This would lead into a breakeven energy price of 0.28 €/kWh. Subsequently, a realistic development of the electrolysers and fuel cell will result in a round trip efficiency of 40 %. The capital and operating costs should be reduced such that energy price becomes 0.10 €/kWh. That way this process would be highly attractive to implement as an energy buffer for fluctuating power.

## 6.Conclusion

It can be concluded that the ammonium bicarbonate/formate system is capable of storing and producing electricity for a price of 0.33 €/kWh. The current round-trip efficiency is 21.1 % and it is clear that the efficiencies of the electrolysers and the fuel cell will have to be increased for better performance. The cost of the storage is too high, and the efficiency is too low. Therefore, the process is currently not able to compete with alternative energy storage methods. Cheaper and more efficient electrolysers and fuel cells need to become available. Together with an increase in the round-trip efficiency, until at least 40% to obtain a feasible process with an energy price of 0.10 €/kWh. The big advantage of this process is that it is not dependent on location and it can deal with the challenge of a fluctuation energy supply.

## Acknowledgements

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