International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 916

ELECTRICITY FROM LOW-GRADE HEAT: INCREASING INDUSTRY EFFICIENCY BY ADSORPTION REVERSE ELECTRODIALYSIS

C. Olkis[1], S. Brandani[1] and G. Santori[1*]

[1] University of Edinburgh, University of Edinburgh, School of Engineering, Institute for Materials and Processes, Sanderson Building,
The King's Buildings, Mayfield Road, EH9 3FB Edinburgh

ABSTRACT

Enormous amounts of low-grade heat 60-90 °C are available from industrial processes that can be converted into electricity by Adsorption Reverse Electrodialysis. This study assesses the concept by using experimental data from an adsorption desalination system at 60 °C. The experimental energy consumption of the adsorption regeneration is used to determine the energy and exergy efficiency of the overall system based on the results of a thermodynamic analysis. The system can achieve exergy efficiencies up to 12 % with solutions that can be used in current membranes. Advanced solutions increase the exergy efficiency to 30-40 % highlighting the great potential of the technology.

Keywords: Adsorption desalination, Closed-loop, Reverse Electrodialysis, Gibbs free energy, Experiments

NONMENCLATURE

Abbreviations	
AD	Adsorption desalination
ADRED	Adsorption Reverse Electrodialysis
Ads	Adsorber
Cond	Condenser
Evap	Evaporator
dist	Distillate
in	Inlet
low/high	Low/high salinity solution
KAc	Potassium acetate
ORC	Organic Rankine Cycle
PRO	Pressure retarded osmosis
RED	Reverse Electrodialysis
out	Outlet
SEC	Specific energy consumption (kJ/kg_w)
TEG	Solid state thermoelectric generation
Symbols	
C	Salt concentration (mol/kg)
F	Salinity solution flow rate (kg/s)
m_w	Mass of water (kg)
Q	Heat (kJ)
R	Real gas constant (J/(mol K))
T	Temperature (°C)
x	Mole fraction (-)
γ	Activity coefficient (-)
ΔG_{mix}	Gibbs free energy of mixing (kJ/mol)
η	Efficiency
Λ	Ratio of total mole (-)

1. INTRODUCTION

Two-thirds of all primary energy are converted into waste heat, where the majority is emitted below 100 °C [1]. These vast amounts of energy cause economic losses and thermal pollution to the environment.

A major current research focus is the conversion of waste heat into electricity and several different technologies have been developed. Organic Rankine Cycles (ORC) and solid state thermoelectric generators (TEG) are two of the most prominent technologies [2]. ORC are a variation of the steam Rankine cycle, but with an organic working fluid like highly toxic R123. The organic fluid enables ORCs to operate at temperatures as low as 80 °C and to achieve exergy efficiencies of more than 50 % [3]. By contrast, TEG are semiconductors producing a current when a temperature difference is applied between both ends of the system [4]. The voltage is directly proportional to the temperature gradient [4].

A different approach are membrane-based systems that generate electricity from a salt gradient between to different aqueous salt solutions [2].

Reverse Electrodialysis membranes (RED) are permeable to salt ions, while the water molecules are retained within the membrane compartment. Ion exchange enables RED membranes to generate electricity directly from the chemical potential [2]. By contrast, Pressure Retarded Osmosis (PRO) membranes are salt rejecting and only permeable for water increasing the pressure first which can then be used for electricity generation in a turbine [5].

Both systems can be combined with a thermal regeneration system in a closed-loop to deploy artificial salt solutions at higher concentrations than seawater.

Reverse Electrodialysis with multi effect distillation has been proposed as thermal regeneration system for large heat sources at higher temperatures achieving exergy efficiencies up to 85 % in a future scenario. The coupling of RED with membrane distillation was reported for smaller heat sources at exergy efficiencies up to 17 % [6]. Reverse Electrodialysis can also be combined with adsorption desalination (ADRED) for the utilization of small heat sources (Fig. 1) [7]. A thermodynamic model analyzed the feasibility of the process for 227 different salts and 10 different adsorption materials [7]. The study identified LiCl as well as MgI_2 as best performing salts in combination with AQSOA Z01 adsorption material or silica gels. It was shown that the system could achieve an exergy efficiency of 45 % in an ideal, best-case scenario neglecting system limitations [7].

There remains a need to further develop ADRED closer towards the real system application.

In this study, we use experimental data from a small-scale adsorption desalinator. An experiment with Siogel silica gel is performed at 60 °C regeneration temperature to obtain the specific energy required to produce distillate. This experimentally obtained specific energy represents a substantial step forward towards the real system. The best performing salts and conditions from the thermodynamic study were combined with the experimental data to assess the energy and exergy efficiency of the system through the Gibbs free energy on the RED membrane side. The use of the Gibbs free energy opens the analysis to advanced salt solutions which are very promising for the process in the future. Moreover, the results are applied to a case study to determine the electric power that can be generated from 6 MW low grade heat of a paper factory to establish a clearer understanding of the potential of ADRED.

2. ADSORPTION REVERSE ELECTRODIALYSIS SYSTEM

2.1 Overview

An Adsorption Reverse Electrodialysis (ADRED) system converts waste heat from an industrial process into electricity as seen in the example in Fig. 1 [7]. High and low salinity solutions connect AD and RED in a closed loop. The RED membranes generate electricity through the salt gradient, whereas the AD process regenerates the salt solutions to their initial salt concentrations. The evaporator increases the salt concentration of the high salinity outlet solution by partial evaporation. This water vapor from the evaporator adsorbs on the silica gel of the adsorber beds and is desorbed and condensed afterwards. The desorption process is driven by the low-grade heat source. The resulting condensed distillate dilutes the low salinity outlet flow from the RED membranes to the initial concentration.

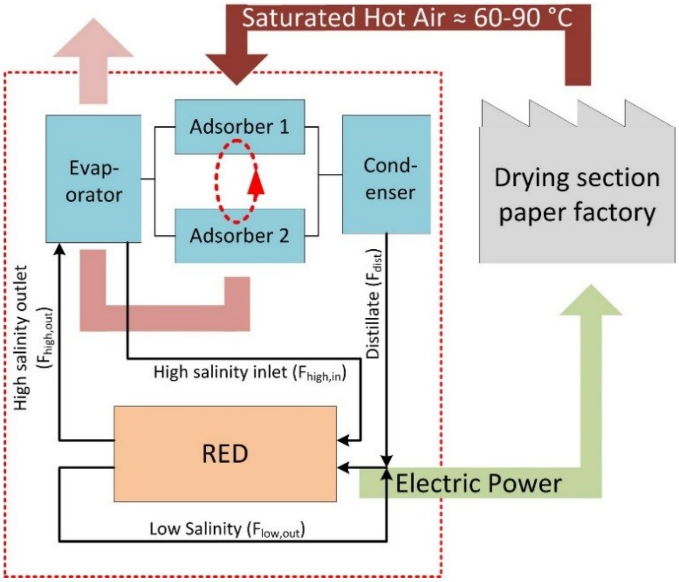

Figure 1 Adsorption Reverse Electrodialysis converts waste heat from a paper factory into electricity.

The assessment of the AD process is entirely based on experimental results. The RED process is based on the same assumptions as the model given in [7], which analyzed the sensitivity of the system's exergy efficiency η_{ex} on the different system variables summarized in table 1. The analysis showed that the exergy efficiency is almost independent from the degree of mixing X [7], because the degree of mixing is a trade-off between the electricity production by RED and thermal energy consumption by AD. The simplest case is X=1, where the two feed streams are entirely mixed $C_{low,out} = C_{high,out}$. In combination with the maximized salt gradient, it can be assumed that $F_{dist} \approx F_{low,in} = F_{high,in}$ and $F_{low,in} + F_{high,in} = F_{high,out}$ (Fig. 1).

Table 1: Overview of system variables and their influence on the exergy efficiency [7]

Property	Symbol	Effect on η_{ex}	Value
Salt gradient	$C_{high,in} - C_{low,in}$	Maximized	C_{lowin} = 0.1m
Heat source temperature	$T_{hot,in}$	Minimized	60 °C
Degree of mixing	X	Independent	1

2.2 *The experimental adsorption desalinator*

The experimental adsorption desalinator [8,9] is shown in Fig. 2 featuring the same components as given in the scheme in Fig.1: An evaporator, two adsorbers and a condenser.

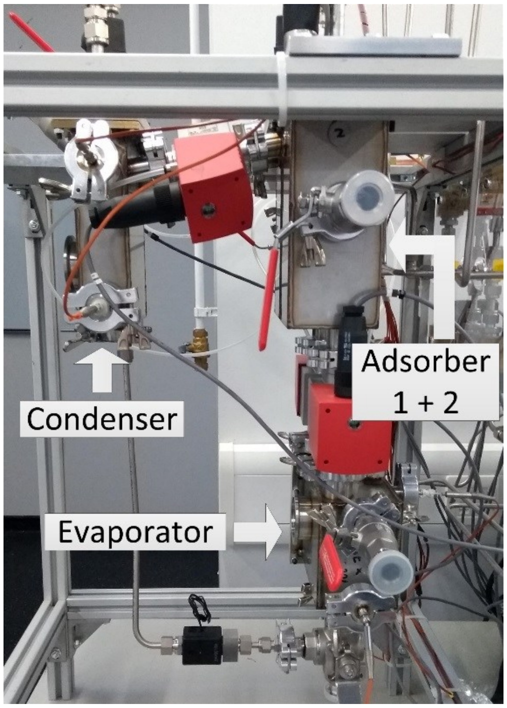

Figure 2: The experimental adsorption test rig [8,9]

Adsorption is a semi-continuous process as one adsorber bed is connected to the evaporator for adsorption, while the other bed is connected to the condenser for desorption at the same time. This ensures that one bed is always desorbing water while the other bed is adsorbing water. During adsorption, the adsorption bed is cooled to ambient temperature, while water vapor from the evaporator adsorbs on the silica gel. After the adsorption phase, the silica gel bed is heated by the low-grade heat source and water desorbs from the material to be condensed on the cold surface of the condenser heat exchanger producing distillate.

An experiment at $T_{hot,in}$ = 60 °C, $T_{cond,in}$ = 25 °C and $T_{evap,in}$ = 30 °C was conducted at 600 s half cycle time, 60 s heat recovery/switching time [8] and Siogel silica gel adsorption material (Oker Chemie GmbH, Germany). This experiment was used to assess the energy input for the adsorption side of the system as well as the water production during this experiment. The results are presented in Fig. 3, where the total heat input for both adsorbers was Q_{ads} = 1655 kJ at 60 °C, while the heat input to the evaporator was Q_{evap} = 1291 kJ at 30 °C and 25 °C ambient temperature to produce m_w = 451 g of water (Fig. 3).

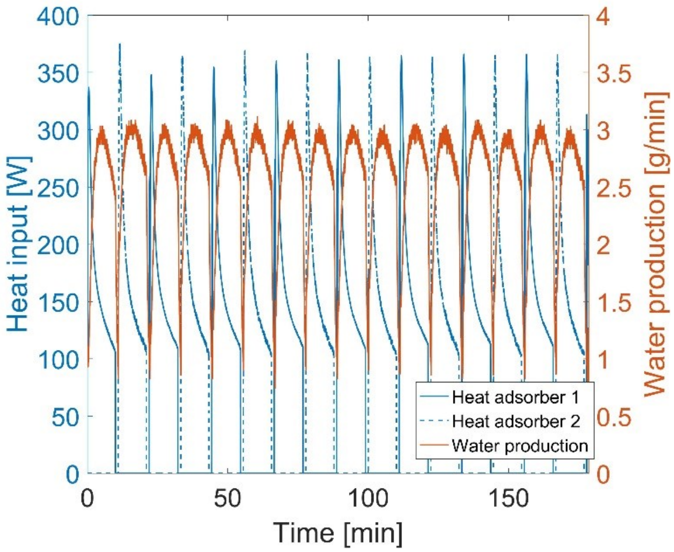

Figure 3: Experimental results of heat input and water production of the experimental system at 60 °C regeneration temperature. The result was used to assess the overall performance of ADRED

The energy input and water production from Fig. 3 are required to determine the specific energy consumption (SEC) (kJ/kg$_{dist}$).

$$SEC_{exp} = \frac{Q_{ads} + Q_{evap}}{m_w} \quad (1)$$

2.3 *Electricity production from Gibbs free energy of mixing*

The Gibbs free energy of mixing (ΔG_{mix}) (kJ/kg$_{mix}$) in eq. (2) is used to assess the electricity production from the RED membrane for the salts given in table 2. The Gibbs free energy of mixing represents the ideal state without limitations of a real membrane like permselectivity and resistances. This is advantageous as current, commercial RED membranes are designed for naturally occurring salt gradients, i.e. NaCl in seawater-river applications, where the salt gradient is less than 1 mol/kg. Current membranes do not work well with artificial solutions of LiCl at very high concentrations or divalent salts like MgI_2. However, the closed loop of the ADRED system allows much higher concentrations than seawater deploying artificial salt solutions and the best possible salts. The best salts were identified in the previous investigation analyzing 227 salts [7] using the Pitzer model [10], where LiCl and MgI_2, where identified as outstanding candidates. Future membranes might be able to operate at very high salinities or with divalent. Thus, they are included in this analysis to point out a way into the future.

$$-\Delta G_{mix} = RT\left\{\left[\sum x_i \ln(\gamma_i x_i)\right]_{low,out} + \left[\sum x_i \ln(\gamma_i x_i)\right]_{high,out} - \Lambda_{low}\left[\sum x_i \ln(\gamma_i x_i)\right]_{low,in} - \Lambda_{high}\left[\sum x_i \ln(\gamma_i x_i)\right]_{high,in}\right\} \quad (2)$$

Where $\Lambda_{low} + \Lambda_{high} = 1$ are the ratios of total moles of the low and high salinity solutions ($\Lambda_{low} = \Lambda_{high} = 0.5$ for equal flows), the activity coefficient γ_i assessed through the Pitzer model [7, 10] and x_i is the mole fraction (-).

Table 2: The selected salts and concentrations where identified in [7, 10]. The low inlet concentration to the membrane is 0.1 mol/kg in all cases.

Salt type	High inlet concentration [mol/kg]	Ref.
NaCl	5	[7]
KAc	8	[11]
LiCl	5	[7]
LiCl	20	[7,12]
MgI_2	5	[7]

2.4 Performance analysis

The energy efficiency of the overall system is described in eq. (4) by the ratio of ΔG_{mix} and the SEC_{exp}. The unit of the SEC represents the energy per mass of distillate and the Gibbs free enrgy of mixing is based on the mass of mixture. Thus, the two flow rates F_{high} and F_{dist} (section 2.1) are needed to obtain the energy efficiency η_{en}.

$$\eta_{en} = \frac{F_{high,out}\Delta G_{mix}}{F_{dist}SEC_{exp}} \quad (3)$$

The exergy efficiency is calculated from the energy efficiency multiplied by the Carnot factor $\eta_c = 1 - T_{cond}/T_{hot}$:

$$\eta_{ex} = \frac{F_{high,out}\Delta G_{mix} m_w}{F_{dist}\left[Q_{ads}\left(1-\frac{T_{cond,in}}{T_{hot,in}}\right) + Q_{evap}\left(1-\frac{T_{cond,in}}{T_{evap,in}}\right)\right]} \quad (4)$$

3. THE SYSTEM PERFORMANCE

The results of the energy and exergy efficiencies of ADRED are shown in Fig. 4. The RED performance was assessed for the salts and concentrations given in table 2. The experimental data for the AD energy takes all system limitations into account.

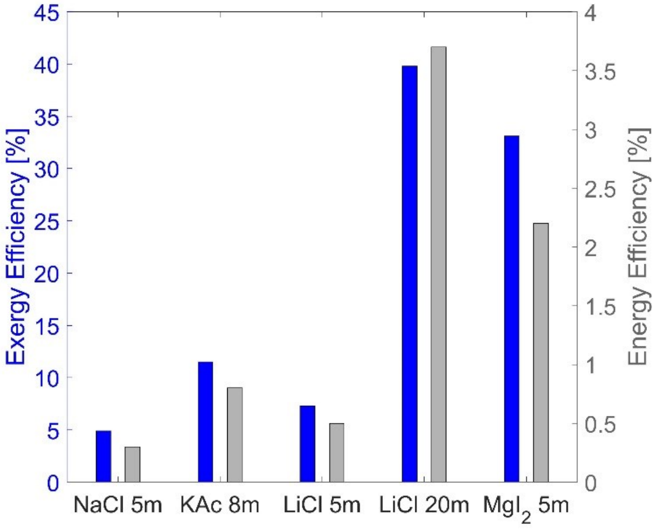

Figure 4: The experimental energy input to the adsorbers and water production for $T_{hot,in}$ = 60 °C, $T_{cond,in}$ = 25 °C, $T_{evap,in}$ = 30 °C, t_{ads} = 600 s and t_{HR} = 60 s. In case of LiCl 20 mol/kg, $T_{evap,in}$ = 50 °C was assumed for the exergy analysis to take the boiling point elevation into account.

In Fig. 4, NaCl and KAc represent two cases achievable with current membrane technology. Here, it is possible to achieve energy efficiencies up to 1 % and exergy efficiencies up to 12 %. By contrast, the advanced salt solutions MgI_2 and LiCl can achieve 2-4 % energy efficiency and almost 30-40 % exergy efficiency. The advanced salts solutions lead to higher ΔG_{mix} (eq. (2)), due to the high activity coefficients of the concentrated solutions [12]. ΔG_{mix} increases by a factor of seven from 5 mol/kg to 20 mol/kg [7,12].

Fig. 4 also confirms the results in the thermodynamic analysis [7], where LiCl at 5 mol/kg achieved an exergy efficiency of 10 % compared to the 7 % using the experimental data for adsorption desalination. The same salt at 20 mol/kg had an exergy efficiency of 43 % in the thermodynamic analysis and 39 % here.

3.1 Case Study: 6 MW heat from paper factory

The results of Fig.4 were applied to a case study based on Fig.1. The example in Fig. 1 shows the application of ADRED to the heat from the drying section of a paper factory [13]. A mid-sized paper factory emits around 6 MW at 60-90 °C of saturated hot air through exhaust fans on the roof. The heat source size and temperatures in this scenario are ideal for the utilization in the ADRED process.

The ADRED system is powered by 6 MW waste heat from the drying section of a mid-sized paper factory. The entire waste heat flow is firstly used for water desorption in the adsorber beds. Afterwards the remaining heat flow passes the evaporator to slightly increase its temperature above the condenser temperature for an improved performance of the silica gel material [7]. This sequence allows a larger ADRED system, because the 6 MW heat flow does not need to be split between evaporator and adsorbers, but the entire heat can be used for desorption.

Fig. 6 shows the power generation from the ADRED system powered by 6 MW of low grade heat considering pumping losses as well. The pumping losses are based on 20 % electricity losses for pumping within the RED stack and between AD and RED [2]. In addition, 5 kJ/kg_{dist} were taken into account for the electricity consumption of an adsorption desalination plant [14]. The results in Fig. 6 show that current membranes with NaCl or KAc solutions generate up to 50 kW considering pumping losses. Advanced solutions improve the electricity generation by almost an order of magnitude to 300 kW in case of LiCl at 20 mol/kg or 170 kW in case of MgI_2 at 5 mol/kg. In addition to the electricity production, water from the saturated hot air will condense when heat is transferred to the ADRED process. This water can be returned to the paper production process reducing its water consumption as in some cases paper factories even have to shut down during summer months due to their high water consumption.

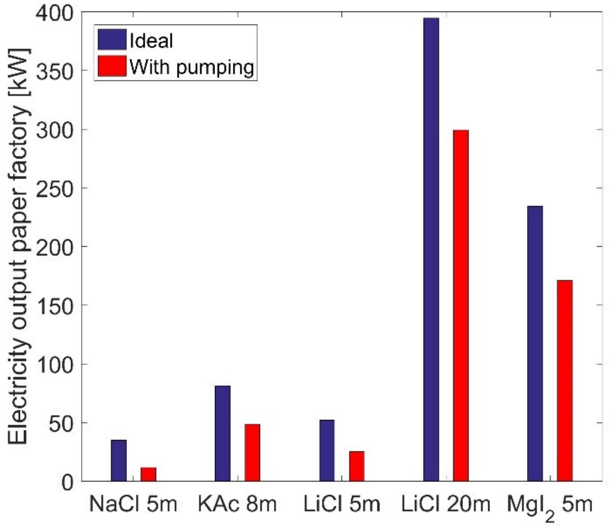

Figure 6: The electric power output of ADRED utilizing the waste heat from the drying section of a paper factory emitting 6 MW of waste heat.

4. CONCLUSIONS

Low-grade waste heat 60-90 °C from industrial processes can be converted into electricity by Adsorption Reverse Electrodialysis. In this study, we assess the performance of the Adsorption Reverse Electrodialysis by using experimental data obtained from a small-scale adsorption test rig. This step advances the investigation closer to the real application. The electricity production of the Reverse Electrodialysis membrane is assessed through the Gibbs free energy of mixing in consistence with the previous study. The results show that the system can achieve energy efficiencies up to 1 % and exergy efficiencies up to 12 % with current solutions. Membranes optimized for advanced solutions could improve the energy efficiency to 2-4 % and the exergy efficiency to 30-40 %, which is an outstanding prospect. A case study shows that Adsorption Reverse Electrodialysis with advanced solutions could generate up to 300 kW of electricity from a 6 MW waste heat source considering pumping losses.

ACKNOWLEDGEMENT

This work was performed within the RED-Heat-to-Power project (Conversion of Low-grade Heat to Power through closed loop Reverse Electro-Dialysis) - Horizon 2020 programme, Project Number: 640667: www.red-heat-to-power.eu.

REFERENCES

[1] Rattner AS, Garimella S. Energy harvesting, reuse and upgrade to reduce primary energy usage in the USA. Energy. 2011 Oct 1;36(10):6172-83.

[2] Tamburini A, Tedesco M, Cipollina A, Micale G, Ciofalo M, Papapetrou M, Van Baak W, Piacentino A. Reverse electrodialysis heat engine for sustainable power production. Applied energy. 2017 Nov 15;206:1334-53.

[3] Shengjun, Zhang, Wang Huaixin, and Guo Tao. "Performance comparison and parametric optimization of subcritical Organic Rankine Cycle (ORC) and transcritical power cycle system for low-temperature geothermal power generation." *Applied energy* 88.8 (2011): 2740-2754.

[4] Riffat SB, Ma X. Thermoelectrics: a review of present and potential applications. Applied thermal engineering. 2003 Jun 1;23(8):913-35.

[5] Post JW, Veerman J, Hamelers HV, Euverink GJ, Metz SJ, Nymeijer K, Buisman CJ. Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis. Journal of membrane science. 2007 Feb 1;288(1-2):218-30.

[6] Micari M, Cipollina A, Giacalone F, Kosmadakis G, Papapetrou M, Zaragoza G, Micale G, Tamburini A. Towards the first proof of the concept of a Reverse ElectroDialysis-Membrane Distillation Heat Engine. Desalination. 2019 Mar 1;453:77-88.

[7] Olkis C, Santori G, Brandani S. An Adsorption Reverse Electrodialysis system for the generation of electricity from low-grade heat. Applied energy. 2018 Dec 1;231:222-34.

[8] Olkis C, Brandani S, Santori G. A small-scale adsorption desalinator. Energy Procedia. 2019 Feb 1;158:1425-30.

[9] Olkis C, Brandani S, Santori G. Cycle and performance analysis of a small-scale adsorption heat transformer for desalination and cooling applications. Accepted Manuscript. Chemical Engineering Journal. 2019 Jun

[10] Pitzer KS, Mayorga G. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. The Journal of Physical Chemistry. 1973 Sep;77(19):2300-8.

[11] Giacalone F, Olkis C, Santori G, Cipollina A, Brandani S, Micale G. Novel solutions for closed-loop reverse electrodialysis: Thermodynamic characterisation and perspective analysis. Energy. 2019 Jan 1;166:674-89.

[12] Robinson RA. The water activities of lithium chloride solutions up to high concentrations at 25. Transactions of the Faraday Society. 1945;41:756-8.

[13] Kong L, Price L, Hasanbeigi A, Liu H, Li J. Potential for reducing paper mill energy use and carbon dioxide emissions through plant-wide energy audits: A case study in China. Applied Energy. 2013 Feb 1;102:1334-42.

[14] Ng KC, Thu K, Kim Y, Chakraborty A, Amy G. Adsorption desalination: an emerging low-cost thermal desalination method. Desalination. 2013 Jan 2;308:161-79.