Methanol-based thermochemical storage for energy-saving district heating networks

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Abstract:

With the increasing volatility in natural gas markets and the need for residential heat, research for alternative fuels is necessary for several regions. This paper presents a high-duration thermochemical energy storage system (TCES) based on methanol, evaluating its integration with district heating networks, offering a renewable solar-based storage solution and low-temperature heat generation from the exothermic discharge reaction heat. The system eliminates greenhouse gas emissions by using concentrated solar thermal energy to decompose methanol into synthesis gas. Applying the optimised operational thermodynamic parameters, it is possible to satisfy the thermal demand of 892 households in Spain through 12 MW of concentrated solar energy supported by 10 hours of energy storage. Storage efficiencies exceeding 30% and chemical conversion efficiencies exceeding 65% have been demonstrated, resulting in a combined efficiency of 55% for the heating network and methanol TCES. The results show a levelized cost of storage (LCOS) highly competitive with other storage systems (<100 €/MWh), given the simplicity and flexibility of the proposed system.

Keywords:

Thermochemical Energy Storage, Methanol, Concentrated Solar Power, District Heating

1. Introduction

Global energy consumption has increased significantly in recent decades [1]. IEA expects that the new renewable installed capacity in the next five years (>2300 GW) will be equivalent to that installed in the past 20 years [2]. Despite this effort to contribute to a clean and sustainable generation [3]–[5], many processes still require thermal power and an energy source constant over time.

The challenges posed by the COP21 objectives [6] regarding the control of the global average temperature increase assume the deployment of a storage capacity of 9000 GWh by 2050 [7]. Currently, sensible heat storage systems (SHS) and latent heat storage (LHTES) have gained commercial capacity [8]–[10], but still have high costs and unavoidable environmental losses. In this regard, thermochemical energy storage systems (TCES) are presented as an alternative. Thermal energy decomposes chemical bonds generating products that can release energy when integrated into a discharge cycle through an exothermic reaction [11]. The versatility and flexibility of the system, given various possible storage strategies, offer an additional solution to TES and phase-change material (PCM) systems [12].

District heating systems distribute heat from a central source, such as a power plant or industrial facility, to multiple buildings in a geographical area [13]. Energy storage can be used in district heating systems to enhance efficiency and reduce their environmental impact [14]. For instance, surplus heat generated by a power plant or industrial facility can be stored in a TES system [15]. This heat can then be used to meet the heating requirements of the buildings in the district during peak demand times, reducing the need to generate additional heat from fossil fuels [16], [17]. Furthermore, energy storage can be used in conjunction with renewable energy sources to provide a reliable heat source for district heating systems [18]–[20]. This can help reduce the dependence on fossil fuels and improve the overall sustainability of the district heating system [21]–[24]. Thermochemical energy storage (TCES) can be used in district heating systems to store and discharge heat from clean energy sources, such as solar or geothermal power [25]–[27]. In this application, methanol is heated to a relatively low temperature (<315 ºC) [28], leading to its decomposition into hydrogen (H_2) and carbon monoxide (CO). The heat produced by the synthesis reaction is then stored in a thermal energy storage system, such as a large tank of water or molten salt [29]. When the stored heat is needed, high-pressure hydrogen gas and carbon monoxide are recombined to produce methanol. This reaction releases heat, which can generate steam and power a turbine to produce electricity [30]–[32] or, as proposed in this work, to support permanent district heating operation. The TCES stores renewable energy and releases it when needed in the system, substituting the boilers. Liu and Yabe [30] proposed a system for transporting energy using methanol, which involves a two-stage process for synthesising methanol in a liquid phase. This

process includes the formation of intermediate products, such as methyl formate, achieving a transportation efficiency of 75% for a conversion ratio. In the study by Bai et al. [29], technical feasibility was evaluated for a 20 kW methanol-based thermal energy storage system consisting of a remodelled parabolic through the collector. A novel system proposed by Rodriguez-Pastor et al. [31] involved the conversion of methanol to methane TCES configuration, from its intermediate step to synthesis gas, obtaining an overall efficiency of 40%.

The advantage of using methanol TCES in district heating systems is that it allows surplus heat generated by renewable energy sources to be stored for later use [32], while methanol can be obtained from cheap and clean feedstocks, such as biomass [33]. Integration of district heating networks with storage further increases overall associated costs, but allows for a reduction in fuel consumption, typically natural gas with volatile prices. This can help to enhance the reliability and stability of the district heating system and reduce the need to generate heat from fossil fuels [34]. Therefore, thermochemical storage is a promising technology for storing and releasing heat from renewable energy sources [35], and its potential to improve the efficiency and sustainability of district heating systems is discussed in this work, by presenting a form of thermal energy generation, which is also storable and without greenhouse gas emissions. In addition, this paper demonstrates that its levelized cost of storage (LCOS) is highly competitive with other TCES systems, given the simplicity and flexibility of the proposed system.

2. System Description

The proposed system (**Figure 1**) makes use of methanol decomposition and synthesis reactions. Thermal integration for the endothermic reaction will be done with a central receiver system and a heliostat field. The liquid pumping of methanol at the inlet of the charge cycle will reduce the compressor power [31], bringing the liquid methanol to 10 bar at the reactor inlet.

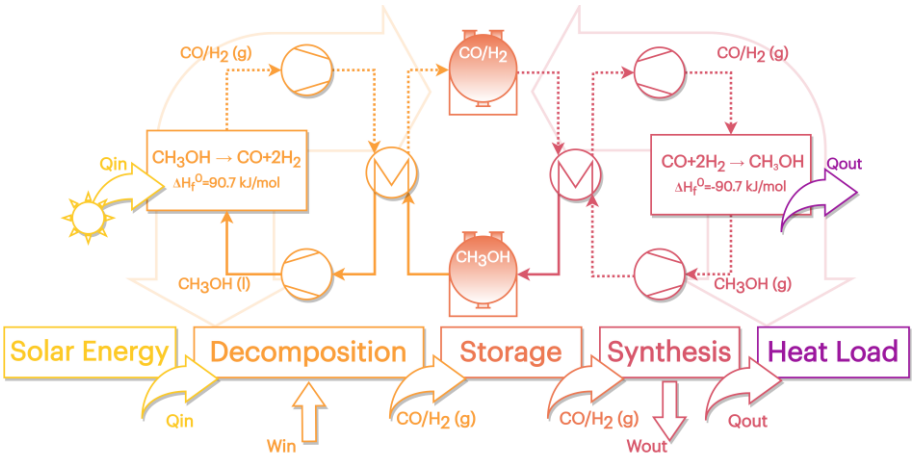

Figure 1. Conceptual process flow diagram of the proposed Methanol-based solar hybrid TCES system.

At the outlet of the charge phase, the synthesis gas (H_2/CO) is stored in tanks, to be discharged into the bottoming cycle, which will synthesise the syngas to methanol at 50 bar. The heat generated in this exothermic reaction will be recovered in a jacket exchanger for the generation of hot water for district heating. The full integration of both charging and discharging cycles is shown in **Figure 2**.

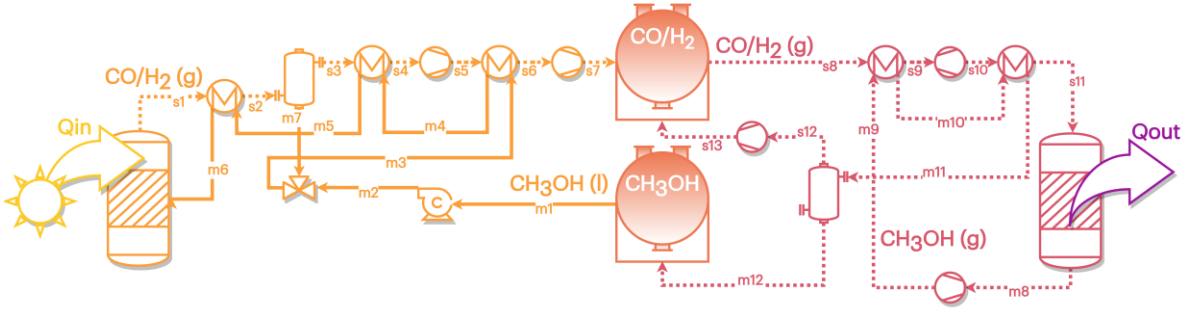

Figure 2. Process flow diagram of the Methanol-based solar hybrid TCES system. m: Methanol, s: Syngas, Qin: Required endothermic heat, Qout: Exothermic heat. Dotted lines: gas-state phase, solid line: liquid-state phase

Methanol-to-syngas conversion can occur in several ways: direct decomposition of methanol [36], steam reforming [37], partial oxidation [38] and auto-thermal reforming [39]. The direct decomposition reaction (Equation 1) is a simple reaction that occurs at temperatures below 350°C [40]. Full methanol conversion is obtained at higher temperatures as the inlet pressure increases.

$$CH_3OH \rightarrow CO + 2H_2 \qquad \Delta H_{298} = 90.7\ kJ/mol \tag{1}$$

Liquid methanol will be pumped into a network of heat exchangers (**Figure 3**), which will use the syngas generated at high pressure and temperature to preheat CH_3OH. Unreacted methanol is separated from a flash separator and recirculating this methanol back into the reactor to ensure complete conversion.

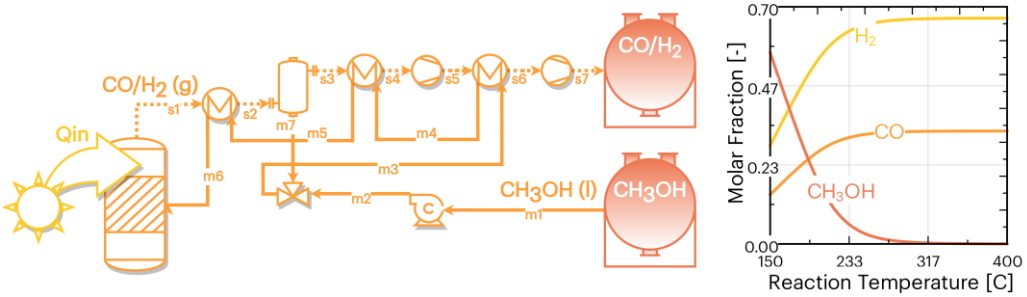

Figure 3. Process flow diagram of the direct solar decomposition of the methanol process (charge phase) and the associated conversion of the molar fraction as a function of reaction temperature. m: Methanol, s: Syngas, Qin: Required endothermic heat. Dotted lines: gas-state phase, solid line: liquid-state phase

The conversion of syngas to methanol releases thermochemical energy. Syngas is produced and stored at 100 bar and ambient temperature, avoiding thermal losses and providing long-term energy storage capability. This paper focuses on the analysis of the former, converting syngas to methanol in a closed-loop approach for TCES systems (Equation 2):

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H_{298} = -90.7\ kJ/mol \tag{2}$$

Syngas-to-methanol (**Figure 4**) is the main route of global methanol production [37]. The reaction occurs in a range of 15-150 bar, 180-300°C, and an H_2/CO ratio< 4.1 [26], [41], catalysed by a standard industrial catalyst ($Cu/ZnO/Al_2O_3$) [42]. This work assumes a quasi-isothermal tubular reactor at 50 bar. The heat released in the exothermic formation of methanol is provided to a heat transfer fluid (HTF) that circulates through a cooling jacket around the reactor [40].

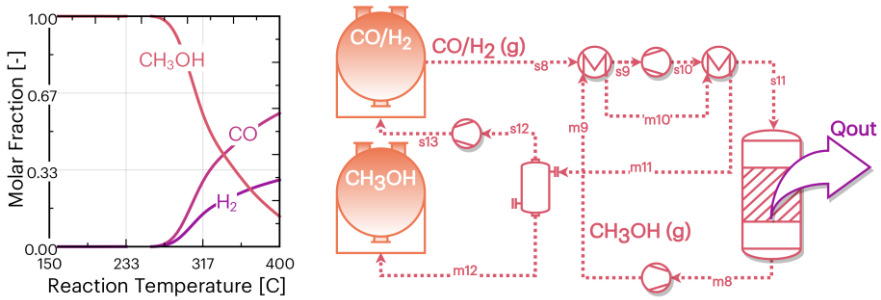

Figure 4. Process flow diagram of the methanol synthesis process (discharge phase) and associated molar fraction conversion as a function of reaction temperature. m: Methanol, s: Syngas, Qout: Exothermic heat. Dotted lines: gas-state phase, solid line: liquid-state phase

3. Simulation

The methanol TCES system has been simulated with the commercial software ASPEN HYSYS [45] using the Peng-Robinson thermodynamic package. The nominal input parameters of the system are shown in **Table 1**. The entire equipment required for the process is well-known in the industry and can be modelled using lumped

volume approaches, as discussed in [43]. However, more detailed kinetics and higher-resolution models maoffer even more precise results [44].

Table 1. Thermodynamic considerations assumed for the simulation of the methanol TCES system.

Variable	Value
Inlet CH_3OH molar flow of the charging process	100 mol/s
CH_3OH storage temperature/pressure	64.67 ºC / 1 bar
Heat Exchangers approach temperature	20 K
Isentropic efficiency of liquid methanol pump	65%
Isentropic efficiency of compressors	89%
Isentropic efficiency of turbines	92%
Endothermic reaction temperature/pressure	315 ºC / 10 bar
Exothermic reaction temperature/pressure	250 ºC / 50 bar
Syngas CO/H_2 storage pressure	100 bar
Discharge pressure	1 bar
Energy storage time	10 hours

Thermodynamic evaluation has been carried out based on the definition of the overall performance (η_{plant}) of the TCES system (Equation 3).

$$\eta_{plant} = \frac{\dot{Q}_{exo} + \dot{W}_T}{\dot{Q}_{CH_3OH} + \dot{Q}_{sol}} \cdot \psi = \frac{\dot{Q}_{exo} + \dot{W}_T}{HHV_{CH_3OH} \cdot \dot{m}_{CH_3OH} + \dot{W}_{PV} + \dot{Q}_{CSP}} \cdot \frac{h_{dis}}{h_{charge}} \quad (3)$$

The performance of the storage system ($\eta_{storage}$) considers the turbine energy outputs in the discharge phase, when considering the solar photovoltaic and thermal input (Equation 4).

$$\eta_{storage} = \frac{\dot{P}}{\dot{Q}_{sol}} \cdot \psi = \frac{\dot{W}_T}{\dot{W}_{PV} + \dot{Q}_{CSP}} \cdot \frac{h_{dis}}{h_{charge}} \quad (4)$$

Chemical conversion (η_{sol-ch}) is described by the solar-to-chemical efficiency, in terms of power (Equation 5).

$$\eta_{sol-ch} = \frac{X_{CH_3OH}\dot{m}_{CH_3OH}\Delta H_{CH_3OH}}{\dot{Q}_{CSP}} \quad (5)$$

Finally, the electrical recovery in the discharge phase turbines is quantified (Equation 6) with the solar-to-electrical efficiency ($\eta_{sol-elec}$) as a function of storage time.

$$\eta_{sol-elec} = \frac{\dot{P}}{\dot{W}_{PV} + \dot{Q}_{CSP}} \cdot \frac{h_{dis}}{h_{charge}} \quad (6)$$

Considering the nominal domestic hot water consumption of a person in the region of Spain, the number of single-family dwellings (4 persons) covered with exothermic heat will be given by Equation 7. The daily by domestic hot water consumption of a person in Spain is estimated to be 28 litres [45].

$$Dwellings = \frac{Q_{exo}/C_p\Delta T}{28} \cdot Persons \quad (7)$$

Where C_p is the specific heat of water (4.184 kJ/kg-K), ΔT is the temperature difference between the cold water return line and the hot water to meet the heat demand, assumed to be 50ºC [46].

Economic analysis depends on the development of component and product markets, which can affect the accuracy of the approximations used to estimate emerging technologies. The expressions presented in **Table 2** form the basis of the economic analysis.

Table 2. Mathematical expressions for estimating equipment costs.

Equipment	Expression	Reference
Compressors	$IC_C = 643.15 \cdot \dot{W}_C^{\,0.9142}$	[47]
Turbines	$IC_T = 4001.4 \cdot \dot{W}_T^{\,0.6897}$	[48]

Pump	$IC_P = 3531.4 \cdot \dot{W}_P^{0.71} \cdot \left[1 + \left(\frac{1-0.8}{1-\eta_{i,P}}\right)^3\right]$	[49]
Heat Exchangers	$C_{HE} = 2546.9 \cdot A_{HE}^{0.67} \cdot p_{HE}^{0.28} \cdot 10^{-6}$	[49]
Cooling Tower	$IC_{Cooling}^{tower} = 32.3 \cdot \dot{Q_{cool}}$	[50]
Endothermic Reactor	$IC_{Dr} = 13140 \cdot \dot{Q}_r^{0.67}$	[51]
Exothermic Reactor	$IC_{Mr} = 19594 \cdot \dot{Q}_r^{0.5}$	[51]
Tanks	$IC_{Tank} = 83 \cdot V$	[52]
Solar Photovoltaic Field	$IC_{PV} = 0.995 \cdot \dot{W}_{PV} \cdot 10^6$	[2]
CSP Tower	$IC_{tower}^{solar} = 57.07 \cdot \Phi_{Receiver}$	[53]

The levelized cost of storage (LCOS) indicator is proposed for the overall economic evaluation (Equation 7), considering a discount rate (r) of 5% and a useful life of the plant (n) of 20 years, and the exothermic reaction energy Q_{exo}.

$$LCOS = \frac{CAPEX + \sum_{i=1}^{n} \frac{OPEX_i}{(1+r)^i}}{\sum_{i=1}^{n} \frac{Q_{exo}}{(1+r)^i}} \quad (7)$$

$CAPEX$ being the initial investment cost of the plant, $OPEX_i$ the annual maintenance costs and Q_{exo} the annual energy produced in the exothermic phase of the synthesis reaction.

4. Results and Discussion

4.1. On-design results

The system design results are shown in **Table 3**. The overall efficiencies obtained for the plant η_{plant} are reduced (<15%) due to the consideration of the methanol input energy and the low exothermic heat of reaction. This fact significantly favours the load cycle since less thermal power is required for the decomposition of methanol to syngas, shown in the solar-to-chemical efficiency η_{sol-ch}, which reaches values above 65%.

Table 3. TCES system results on design for nominal operating parameters.

Parameter	Value
Solar-to-chemical efficiency (η_{sol-ch})	0.677
Solar-to-electrical efficiency ($\eta_{sol-elec}$)	0.071
Overall performance (η_{plant})	0.125
Storage performance ($\eta_{storage}$)	0.356
Required endothermic reaction heat [MW] ($\dot{Q}_{endo}$)	12.658
Exothermic reaction heat [MW] ($\dot{Q}_{exo}$)	-8.686
Dwellings covered	892
Covered annual heat demand [MWh]	53445
CAPEX [M€]	19.72
OPEX [M€]	0.936
LCOS [€/MWh]	85.61

On the other hand, the storage efficiency of the system $\eta_{storage}$ shows competitive values, exceeding 35%, given the recovery of the syngas decompression in the discharge cycle turbines and the reduced PV power output after thermal integration of the streams. With the 9 MW obtained at the output of the synthesis reactor, the demand for 892 single-family houses or the equivalent of a rural village can be covered. Thus, the initial investment of the plant is almost 20 M€, after considering an annual OPEX of almost one million euros in operating and maintenance costs of the plant. This value is lower in terms of fuel consumption compared to District Heating systems based on other fuels [34], although the cost assessment of the heat network has not been considered in this paper. The levelised cost value, LCOS, has been shown to be 60% lower than molten salt systems and competes with future predictions of hydrogen-based storage systems (90-160 €/MWh) [54].

Figure 5 shows the main thermal currents of the system, based on the above thermodynamic assumptions and considerations. Thus, a large amount of energy is returned to the methanol storage, given the low efficiency of the synthesis reactor. This high value is due to the high calorific value of methanol, which is not utilised given the low heat of the synthesis reaction. Heat exchanger losses are assumed to be 3%, and solar field losses are assumed to be 30%.

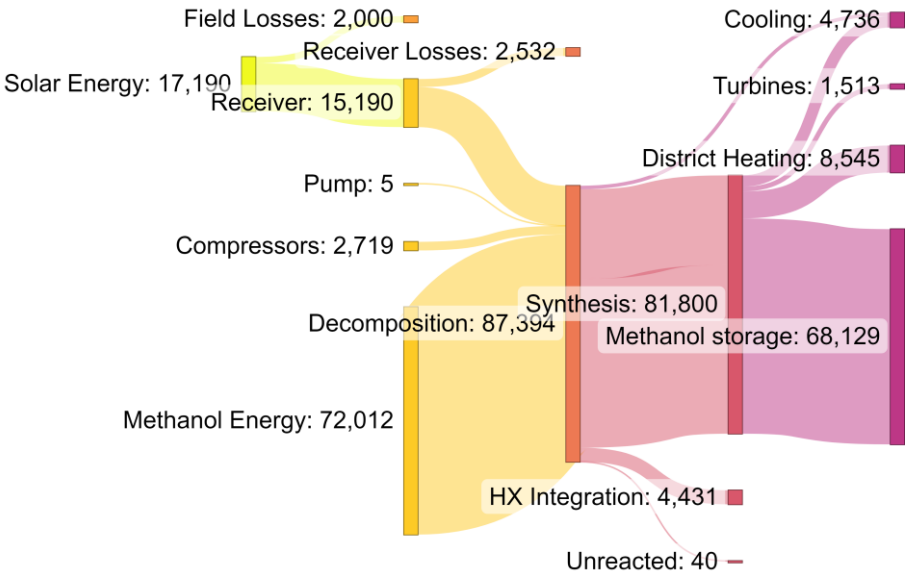

Figure 5. Sankey diagram for the nominal operating conditions of the methanol-TCES system.

Therefore, the solar photovoltaic field will feed 3 MW of compressor and pump consumption and 15 MW of receiver solar power will be required to extract 8.5 MW for the heat network. The efficiency in terms of solar power and DH power will be 47%, whereas the combined efficiency of cogeneration, considering the energy exported from the turbines, will be 55%, 40% lower than in internal combustion reciprocating engines [55].

4.2. Sensitivity analysis

The variation in thermal power from the solar receiver will be crucial in the sizing of the reactor and its auxiliary systems. **Figure 6** evaluates the variation in efficiency as a function of the endothermic temperature of direct CH_3OH decomposition. Chemical conversion efficiency reaches a maximum at intermediate reaction temperatures, although complete conversion cannot be ensured because of a higher molar enthalpy drop in the reactor and an increase in yield. However, maximum decomposition conversion is required for solar-to-electrical yields to ensure better utilisation in the gas turbines of the discharge cycle. This also applies to the overall plant performance, which will be higher as the methanol inlet pressure decreases, i.e., to ensure complete conversion to syngas.

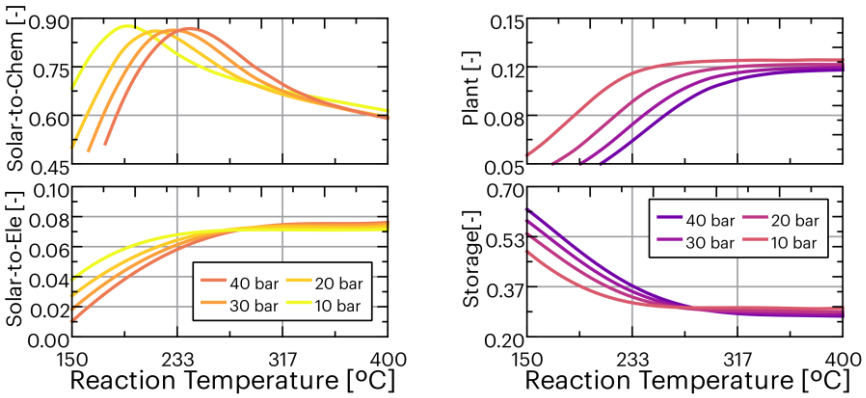

Figure 6. Solar-to-Chemical/Solar-to-Electrical yields on the left, and plant and storage yields (overall) as a function of direct methanol decomposition reaction temperature on the right.

This trend is also reflected when evaluating the performance of the heat network (**Figure 7b**), where higher reaction temperatures (right) will result in greater synthesis gas generation and consequently greater conversion in the exothermic reactor. The increase in covered households for a reaction temperature between 150-250ºC is 650 households, which then stabilises at the nominal value of close to 900 homes with the studied characteristics.

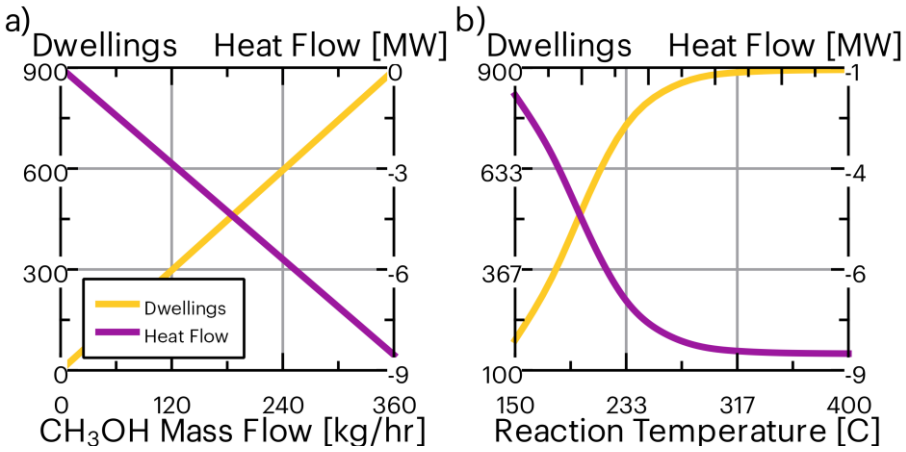

Figure 7. Number of dwellings covered (thermal demand) and exothermic power generated in the synthesis reaction as a function of a) methanol mass flow rate at the inlet of the charging process and b) reaction temperature of the direct decomposition of methanol.

The effect of the mass flow rate of methanol at the inlet is linear with respect to the exothermic power, where for every 120 kg/hr of methanol in the system, the demand of approximately 300 homes is covered (**Figure 7a**).

4.3. Economic Analysis

One of the most remarkable parameters of the proposed system is its low-levelized storage cost, optimised under nominal conditions to be minimal and achieve maximum overall yields. **Figure 8** shows the variation of the LCOS with respect to the operating conditions of the charging phase (**Figure 8a**) and the discharging phase (**Figure 8b**). Opposite trends are obtained, where higher decomposition reaction temperatures result in lower costs, given a higher thermal energy supply to the heat network.

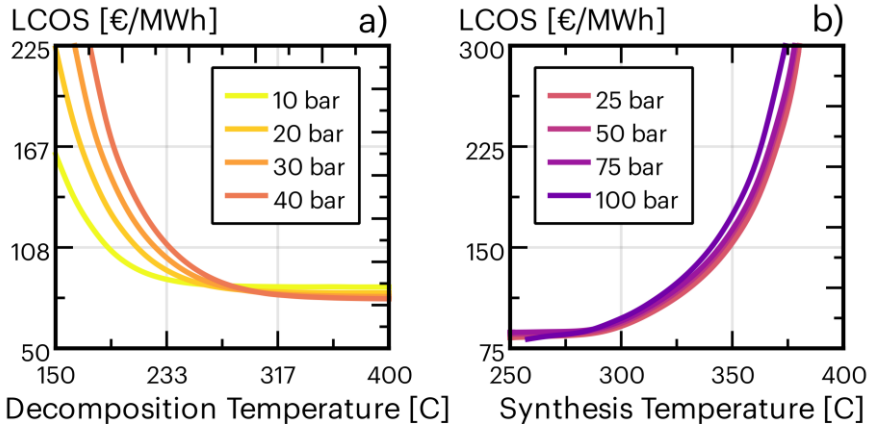

Figure 8. Levelised cost of storage as a function of a) direct methanol decomposition temperature and b) syngas to methanol synthesis temperature.

This LCOS is even lower for higher liquid methanol pressures due to lower compressor consumption. This trend is opposite in the case of the synthesis reaction, where higher temperatures result in lower conversion and lower exothermic energy, and higher pressures imply higher associated conversions but with less influence than in the case of the charging phase.

5. Conclusions

This paper proposes a high-duration thermochemical storage system based on methanol, which evaluates its integration with district heating networks, offering a renewable solar-based storage solution and low-temperature heat generation from the exothermic discharge reaction heat:

i) The system eliminates greenhouse gas emissions by using concentrated solar thermal energy to decompose methanol into synthesis gas.
ii) Given the low heat of the direct methanol decomposition reaction, chemical conversion efficiencies in the charging phase are greater than 65%.
iii) Storage efficiencies are greater than 35%, producing 8.5 MW of exothermic power from 15 MW of solar input that decomposes 100 mol/s of methanol.
iv) The proposed configuration serves 892 4-person single-family homes and can cover a rural town with green methanol.
v) Levelized storage costs are 60% lower than molten salt systems, as the system is simple and has a high associated energy density.
vi) An optimal decomposition temperature of 315°C/10 bar and 250°C/50 bar is demonstrated in the exothermic phase, striking a balance between demand coverage and the levelized cost of the system.

Acknowledgements

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Nomenclature

c_{p} specific heat, J/(kg K)
$\dot{m}$ mass flow rate, kg/s
T temperature, °C
X molar fraction, [-]
Q heat energy, [kWh]
W power energy, [kWh]
$\dot{Q}$ heat power, [kW]
$\dot{W}$ power, [kW]

Greek symbols

η efficiency
ψ discharge/charge hours ratio

Subscripts and superscripts

CH_3OH methanol
exo exothermic
$endo$ endothermic
$sol-ch$ solar-to-chemical
$sol-ele$ solar-to-electrical

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