I&EC research
Industrial & Engineering Chemistry Research

pubs.acs.org/IECR

Article

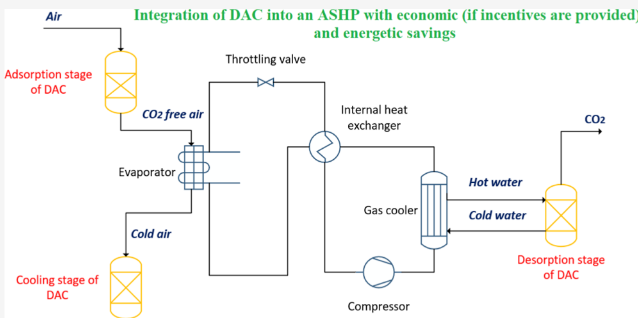
Innovative Process Integrating Air Source Heat Pumps and Direct Air Capture Processes

Grazia Leonzio* and Nilay Shah

Cite This: *Ind. Eng. Chem. Res.* 2022, 61, 13221−13230

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: Most integrated assessment models indicate a need for technological carbon dioxide removal from the atmosphere to achieve climate mitigation targets. Currently, direct air capture (DAC) appears to be one the "backstop" technologies suitable to provide this service. These technologies usually require low-carbon heat as part of their operation cycle. Here, we consider a way of providing this heat when no local heat source is available. Air source heat pump (ASHP) water heaters are a well-known technology that takes heat from the air to supply hot water. Variations on their operating conditions could provide water at 100 °C, when a trans-critical cycle is used. This level of temperature is required by several DAC adsorption processes as the thermal energy for the regeneration stage. For this reason, an innovative process integrating an ASHP and a DAC adsorption system is proposed here. The heat pump provides not only heating but also cooling, while three separate stages (adsorption, cooling, and regeneration) are considered for the DAC. In the integrated process, the air is sent to the adsorbent bed at first and after that to the evaporator of the heat pump and then used for the cooling stage. The hot water supplied by the heat pump is used for the desorption. Different working fluids (CO_2, CO_2-ethane, CO_2-R41), with low ozone depletion and global warming potentials, are investigated. The results show that a high level of efficiency is possible for heat pumps supplying hot water at 100 °C. Moreover, energetic advantages are present with reference to the base case, where heat is provided by a municipal water incinerator and cooling by a cooling tower. Savings in the energy consumption of 55, 60, and 53% for the integrated process using CO_2, CO_2/R41, and CO_2/ethane, respectively, are possible. Economic benefits are present when economic incentives are provided, ensuring lower costs up to 39 \$/tonCO_2, and the technology benefits from location flexibility as only a power supply (and not a heat source) is required.

1. INTRODUCTION

Currently, energy consumption and environmental problems are critical concerns in industrial and social development. Global energy consumption continues to increase, with an average of around 1−2% per year,[1] while carbon dioxide (CO_2) emissions were estimated to be more than 33 Gtons in 2018.[2] Fossil fuels are still the main source used to satisfy the energy demand, leading to environmental problems, such as global warming and climate change.[3]

This problem continues to drive innovation in more high-efficient and low-emission energy technologies for sustainable development.[4]

In this context, heat pumps have been recognized as an efficient and clean technology for heat and cold supplies.[5] It was established that "Heat pumping technologies are a mature, widely deployed, and cost-effective energy efficiency option, with a significant role to play in portfolios of measures to address key energy policy concerns".[6]

Among this technology, renewable heat pumps use the low-grade heat of air, water, or soil to produce heat at a higher temperature, only consuming electricity. In this contest, air source heat pumps (ASHPs) have received much attention due to their simpler configuration and lower installed cost.[7−10] This kind of system is widely used for heating and can extract heat from the air to heat air (air-to-air) or water (air-to-water) for hot water generation.

These systems could supply more than 90% of global water heating with CO_2 emissions lower than that of a traditional gas boiler operating at 92−95% efficiency.[11] Moreover, an ASHP can provide the same hot water with 2 or 3 times higher efficiency compared to a traditional boiler using fossil fuels or an electric water heater.[12] For this reason, the attention of the research community has been focused on ASHP water heaters providing hot water at a temperature lower than 100 °C.

Several thermodynamic cycles, such as vapor compression, cascade, trans-critical, with vapor injection solution, absorp-

Received: May 23, 2022
Revised: August 18, 2022
Accepted: August 18, 2022
Published: August 25, 2022

tion, or heat recuperative, have been investigated for an ASHP.[13−16] The integration with thermal energy storage systems and solar energy is also proposed in the literature in order to improve the efficiency.[17,18]

The trans-critical cycle is the most investigated in the literature for ASHP water heaters, able to supply hot water up to 90 °C. Most of the trans-critical ASHPs use CO_2 as the working fluid, being a natural refrigerant, non-flammable and non-toxic, with zero ozone depletion potential (ODP) and negligible global warming potential (GWP).[19] CO_2 is considered as a perfect working fluid for air conditioning systems, heating, and heat pump water heaters by Lorentzena and Pettersen[20] due to low power consumption and cost and good compactness when it operates in the trans-critical region.

Hot water temperatures up to 60 °C are achieved by a CO_2 trans-critical ASHP in the work of Hu et al.,[21] Wang et al.,[22] Boccardi et al.,[23] and Liao et al.[24] In Hu et al.,[21] the extremum seeking control strategy is proposed in order to minimize the compressor energy instead of maximizing the coefficient of performance (COP). The authors find that supplied water of 60 °C is provided with a good efficiency (a COP of 3.3). A sensitivity analysis is conducted by Wang et al.,[22] evaluating the effect of gas cooler area and discharge pressure on the COP and heat yield. It is found that for hot water of 60 °C, the maximum COP value is 4.2. Liao et al.,[24] finding a maximum temperature for the supplied water of 60 °C, report that an optimal value of COP occurs at an optimal heat rejection pressure, depending on the gas cooler outlet temperature, evaporation temperature, and compressor performance. With the aim to improve the efficiency, the use of multi-ejectors is proposed in Boccardi et al.:[23] a sensitivity analysis is conducted at different ejector areas, compressor frequencies, and ambient temperatures.

Hot water temperatures higher than 60 °C are reported in the literature for a trans-critical ASHP. In Dai et al.,[15] the hot water temperature of 65 °C is ensured with a good COP of 3.35 in a trans-critical cycle using CO_2. The same water temperature with a COP of 3.6 is provided by the same cycle in the work of Saikawa and Koyama,[25] indicating a better efficiency compared to other systems using different refrigerants (R134a, R22, R410A, R407C, R32, propane, isobutane, and propylene).

For a CO_2 trans-critical cycle, a temperature for the supplied hot water of 70 °C is achieved in Nicholas et al.,[26] but with a lower COP value (2.8) compared to the previous works. From a sensitivity analysis, the authors find that a higher efficiency in terms of COP can be obtained at higher ambient temperatures and lower hot water temperatures. The same level of temperature for the supplied water is achieved in a combined system integrating a CO_2 trans-critical cycle with an R134a sub-cooling cycle, as in Song and Cao.[27]

In the work of Lu et al.,[28] a maximum outlet water temperature of 75 °C is obtained for a maximum COP value of 2.88 at an ambient temperature of 10 °C. The same hot water temperature is measured in Laipradit et al.,[29] evaluating the effect of the compressor rotational speed, inlet water temperature, inlet air temperature, and the mass flow rate ratio of water to refrigerant on the heat pump performance.

Moreover, water temperatures up to 80 °C are ensured in Wang et al.,[22] Nekså,[30] Anstett,[31] and Minetto[32] by using a CO_2 trans-critical ASHP. In Wang et al.,[22] it is found that the outlet water temperature has a negative effect on the COP, setting the air temperature as a fixed parameter. On the other hand, fixing the outlet water temperature, the ambient air has a positive effect on the optimal discharge pressure. Minetto[32] finds that a COP value of 2.86, 3.22, and 2.96 is obtained, respectively, from an inlet air temperature of 9.7, 18.3, and 17.2 °C and an outlet water temperature of 80 °C. A similar COP value is suggested by Anstett[31] for a CO_2 trans-critical heat pump providing hot water at 60−80 °C with a COP between 2 and 5.

However, the highest temperature (90 °C) for water achieved in a CO_2 trans-critical ASHP is obtained in Nekså et al.[33] and Zhu et al.[34] In Nekså et al.,[33] the COP is evaluated under different operating conditions and it is found that the CO_2 refrigerant allows higher COPs and hot temperatures compared to other working fluids. Zhu et al.,[34] by using the ejector strategy, obtain a COP of 3.3 when water at 90 °C is supplied and a COP of 4.6 when water is provided at 70 °C. A different refrigerant is used in Yu et al.:[35] the authors use the refrigerant zeotropic mixture R32/R290 that under trans-critical conditions is able to provide water at 90 °C. The positive effect of an internal heat exchanger on the COP is also demonstrated.

The above literature analysis indicates that ASHPs with a trans-critical cycle can provide hot water up to 90 °C from a large air flow rate. It is evident that a small variation in the operating conditions of the cycle could provide hot water at a higher temperature of 100−110 °C.

This thermal energy could be used in different chemical processes, such as in the emerging direct air capture (DAC) technology, which requires a large energy consumption and air flow rate to remove CO_2 from the atmosphere, due to the dilute nature of CO_2 in the air (e.g., a concentration of 400 ppm). Absorption, adsorption, mineral carbonation, membrane, photocatalysis, cryogenic separation, electrochemical approaches, and electrodialysis are the technologies investigated in the literature for DAC.[36−42] Absorption and adsorption are the most investigated and mature processes in this context.

Currently, DAC companies are based on absorption (Carbon Engineering), adsorption (Climeworks, Global Thermostat, Antecy, Hydrocell, Skytree), and ion-exchange resins (Infinitree). Climeworks is the company with the first commercial plant, in Switzerland (Hinwil).[43]

In our previous work, we develop a mathematical model for the DAC adsorption process using different sorbents (metal−organic frameworks and amine-functionalized sorbents) and we compare our results with those of the Climeworks company, who use the APDES-NFC-FD sorbent [3-aminopropylmethyldiethoxysilane (APDES) on nanofibrillated cellulose (NFC)], as in our work.[44] These adsorption systems require thermal energy at 100 °C for the regeneration stage, which is provided by a municipal waste incinerator (MWI), as in Climeworks. On the other hand, cooling for the cooling stage is provided by cooling water. A large air flow rate is needed to capture CO_2 too. However, in order to improve the efficiency of DAC and provide locational flexibility, thermal energy could be provided by an ASHP.

According to these considerations, we propose here a new process integrating an ASHP with a trans-critical cycle into a DAC adsorption process using the APDES-NFC-FD sorbent and investigated in our previous research.[44] We use a trans-critical and not sub-critical cycle because the first one is the most investigated in the literature for an ASHP producing hot water at high temperatures. The heat pump provides cooling

https://doi.org/10.1021/acs.iecr.2c01816
Ind. Eng. Chem. Res. 2022, 61, 13221−13230

and heating for the DAC. Then we extend the outcomes identified in the literature by developing ASHP cycles able to supply hot water at 100 °C. Moreover, this type of integration has not been proposed in the literature. In this analysis, we compare different working fluids (CO_2, CO_2-ethane, CO_2-R41) with a low value of global working potential and ozone depletion. The growing international emphasis on global warming phenomena (driven by the Kigali amendment to the Montreal Protocol) has moved the interest of the manufacturers as well as the scientific community to low-GWP refrigerants.[23] For the proposed integrated schemes, we conduct sensitivity analyses to evaluate the effect of some operating parameters, and we carried out an energetic and economic analysis to estimate the advantages of this process compared to the base case scheme.

2. MATERIALS AND METHODS

2.1. Description of ASHPs and KPIs. In this research, trans-critical ASHPs are considered with different working fluids. Figure 1 shows the schematic diagram of a trans-critical

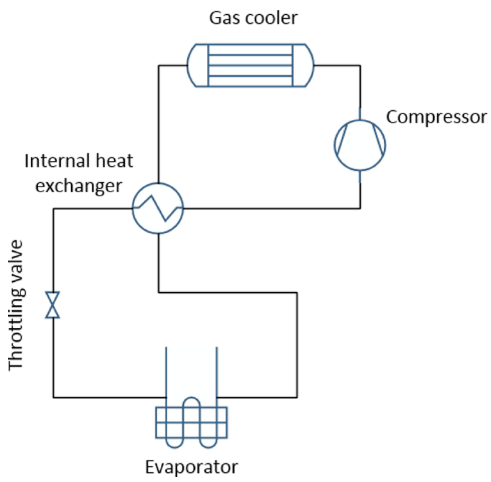


Figure 1. Diagram scheme of an ASHP with a *trans*-critical cycle.

cycle composed of an evaporator, gas cooler, compressor, expansion valve, and internal heat exchanger. An internal heat exchanger is used to improve the performance of the overall system that takes heat from the air through the evaporator and transfers it to the water through the gas cooler for the heating purpose.[45,46]

CO_2/ethane (0.78/0.22 mass fraction), CO_2/R41 (0.5/0.5 mole fraction), and CO_2 are the refrigerants for the trans-critical heat pumps. Table 1 reports the values of critical temperature and pressure for these working fluids.

The refrigerant mixture CO_2/ethane and CO_2/R41 are characterized by no ODP and low GWP.[47,48] Ethane and R41 would improve the efficiency of CO_2, while CO_2 would minimize the drawback of flammability and reduce the GWP of other refrigerants. CO_2, as a natural refrigerant, is non-flammable and non-toxic, with zero ODP and negligible GWP. These refrigerants are used here because they are suggested in the literature for ASHPs in Wang et al.[49] (CO_2/ethane), Wang et al.[50] (CO_2/R41), and Nekså et al.[33] (CO_2), ensuring good values of the COP.

Table 1. Critical Temperature and Pressure for the Refrigerants

	CO_2	CO_2-R41	CO_2-ethane
critical temperature (°C)	31.1	37.6	18.04
critical pressure (bar)	73.8	66.4	60.603

For the considered heat pumps, the most important KPIs such as the operating costs (OPEX), primary energy consumption (E_p), and CO_2 emissions (M_{CO_2}) are evaluated according to the following equations (see eqs 1−3)

$$Ep_{heatpump} = Q_{th} d \frac{ep_{el}}{COP} \quad (1)$$

$$OPEX_{heatpump} = Q_{th} d \frac{c_{el}}{COP} \quad (2)$$

$$M_{CO2\,heatpump} = Q_{th} d \frac{m_{el}}{COP} \quad (3)$$

where ep_{el} is the primary energy of electricity (MJ/kW h_{el}), d is the yearly operating hours of the process (h/year), Q_{th} is the heat power (kW),c_{el} is the electricity price ($/kW h_{el}), m_{el} is the CO_2 content of electricity (kgCO_2/kW h_{el}), and COP is the coefficient of performance, which is the ratio between the heating capacity and input power at the compressor (e.g., electric power). These KPIs are evaluated per kW h_{el} assuming, for the above parameters, values related to the electricity grid of the Switzerland country: c_{el} of 0.13 $/kW h_{el}, m_{el} of 0.171 kgCO_2/kW h_{el}, and ep_{el} of 7.497 MJ/kW h_{el}.

2.2. Conventional DAC Adsorption System. The DAC adsorption process is presented in Leonzio et al.,[44] considering the geometry of a single adsorbent module defined by Climeworks (area footprint excl. options of 20 m^2, with a length of 3.2 m) and an air flow rate of 2.86 m^3/s.[51] The APDES-NFC-FD sorbent, the same cellulose-based amine-functionalized sorbent used by Climeworks for its plant, is considered for the DAC system. In the base case process, CO_2 is captured from the air, having a CO_2 concentration of 400 ppm, by the sorbent bed and it is released after a variation of temperature as a temperature swing adsorption (TSA) process (the adsorption temperature is 25 °C, while the regeneration temperature is 100 °C, as in the Climeworks plant[52]). Cooling water is used for the cooling step, while electricity for fans and heat for the regeneration step are provided by an MWI, as in the Climeworks plant. Table 2 shows the main operating conditions, energy consumptions, data for the adsorbent bed and sorbent, and costs for the conventional DAC process.[44]

2.3. Process Scheme Integrating the DAC Adsorption and ASHP. Considering the energy consumption of DAC, the

Table 2. Main Data of the Investigated DAC System Using the APDES-NFC-FD Sorbent[44]

captured CO_2 (kg/day)	152
adsorption temperature (°C)	25
desorption temperature (°C)	100
heat of adsorption (J/molCO_2)	60000
APDES-NFC-FD particle diameter (m)	0.005
APDES-NFC-FD particle density (kg/m^3)	55.4
height of the bed (m)	3.2
area footprint excl. options of the bed (m^2)	20
electrical energy (kW h_{el}/tonCO_2)	299
regeneration energy (kW h_{th}/tonCO_2)	1427
total costs ($/ton$CO_2$)	751

https://doi.org/10.1021/acs.iecr.2c01816
Ind. Eng. Chem. Res. 2022, 61, 13221−13230

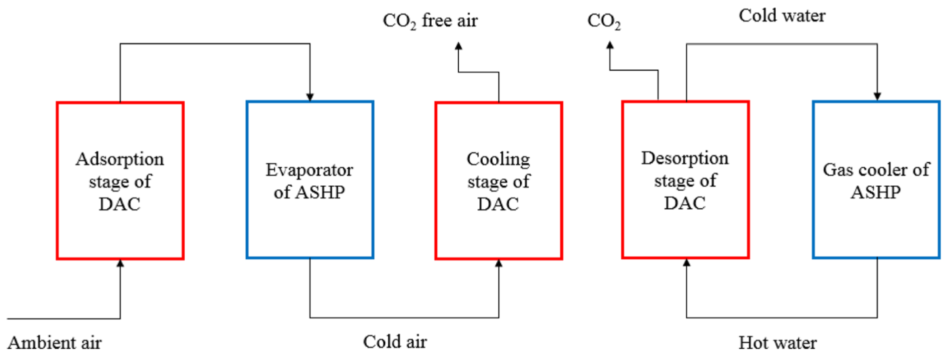


Figure 2. Diagram scheme of the process integrating the DAC adsorption with an ASHP.

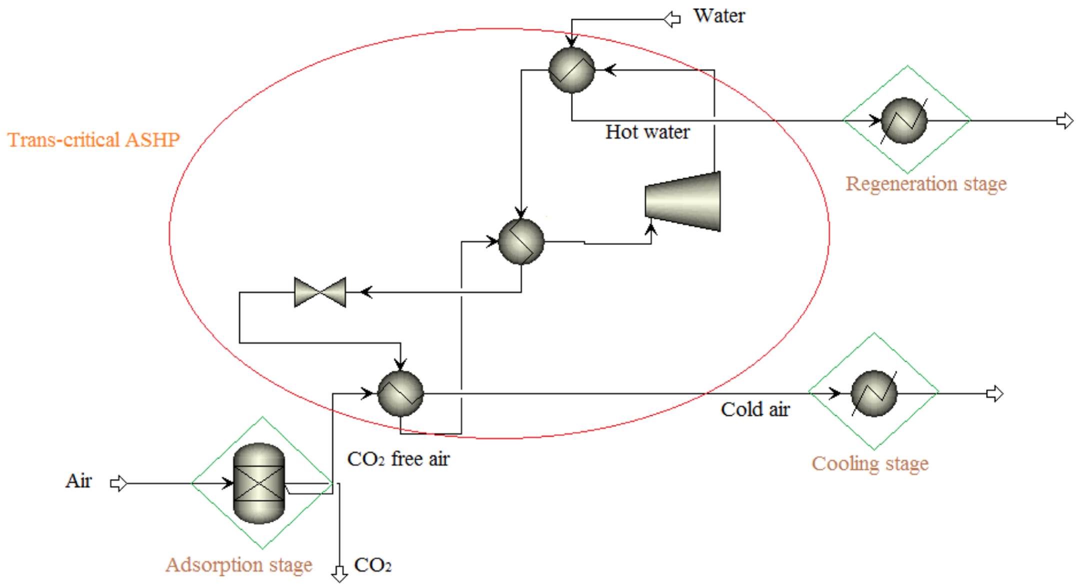


Figure 3. Process scheme in Aspen Plus for the *trans*-critical ASHP integrated in the DAC system.

single scheme of the DAC adsorption and ASHP, we propose the following integration process. In the DAC adsorption system, three separate stages, namely, adsorption, regeneration, and cooling, are considered. CO_2 is adsorbed at 25 °C in the adsorption stage; after that, it is desorbed by supplying heat to the bed at 100 °C, and then the bed is cooled to 25 °C to allow another cycle according to a TSA design. In the overall integrated process, the air is sent to the adsorber for CO_2 removal and then to the evaporator of the ASHP. The outlet air here has a temperature of 15 °C (this value is suggested for the cooling fluid in the Climeworks plant[52]) so that it can be used in the cooling stage of the adsorbent bed. Air for cooling is used by another DAC company, as Anteny,[52] indicating that our proposed scheme is technically feasible and avoids the use of cooling water that Leonzio et al.[44] demonstrate to have a high impact on the operating costs. On the other hand, the hot water supplied from the ASHP at 100 °C is used for the regeneration of the bed, avoiding the use of an MWI as in the base case scenario. Hence, the ASHP is able to cool and heat the adsorbent bed. Figure 2 shows the process flow diagram of the integrated process, while Figure 3 shows the integrated process simulated in Aspen Plus.

The thermodynamic model Soave−Redlich−Kwong is used for these simulations in Aspen Plus because it is well known to be simple and efficient for these types of fluids.[53] The adsorbent bed is simulated through a component separator, eliminating CO_2 from the air, considering the results reported in Leonzio et al.[44] for the DAC system using the APDES-NFC-FD sorbent. Heat exchangers, compressors, and valves are used to reproduce the heat pumps in Aspen Plus.

The ASHPs are simulated considering the data shared in the literature for the thermodynamic cycle (Wang et al.[49] for the CO_2/ethane-based cycle, Wang et al.[50] for the CO_2/R41-based cycle, and Nekså et al.[33] for the CO_2-based cycle) but increasing the compressor ratio in order to supply water at a temperature of 100 °C, required for the DAC regeneration. In particular, the low cycle temperature and pressure of heat pumps are as in the literature, while the high cycle temperature and pressure are obtained from the simulation by increasing the compressor ratio to the appropriate level. Table 3 reports data for the low cycle level of the investigated ASHPs.[33,49,50]

Based on the above data, the integrated ASHPs are designed using Aspen Plus: by knowing the temperature and flow rate of the air coming from the adsorber, it is possible to find the

Table 3. Low Cycle Temperature and Pressure for the Investigated Heat Pumps

	CO_2	CO_2-R41	CO_2-ethane
low temperature (°C)	0	5.39	0
low pressure (bar)	35.11	30.9	32.9

https://doi.org/10.1021/acs.iecr.2c01816
Ind. Eng. Chem. Res. 2022, 61, 13221−13230

refrigerant flow rate that ensures an air temperature at the outlet of the evaporator of 15 °C. By setting a defined compressor ratio, the refrigerant pressure and temperature at the inlet of the gas cooler are defined, while the refrigerant conditions at the outlet of the gas cooler are reported in the literature (45 °C for the ASHP using CO_2/R41, 85 °C for the ASHP using CO_2/ethane, and 10 °C for the ASHP using CO_2).[33,49] These data are used to determine the water flow rate after setting up its supplied temperature.

Two heat exchangers are used to simulate the regeneration and cooling stages of the adsorption system, where the hot water from the gas cooler and cold air from the evaporator are sent, respectively. This allows us to determine whether there is a surplus or deficit of heat during the desorption and to calculate the air temperature at the end of the cooling stage.

An economic analysis is conducted according to the procedure suggested by Peters and Timmerhaus,[54] evaluating capital (CAPEX) and operating (OPEX) costs. For the DAC adsorption system, the economic analysis is shown in Leonzio et al.,[44] while here, the economic analysis for heat pumps is added considering the integrated process. The equipment cost of ASHPs is evaluated by using the Matches program.[55] These costs are based on 2014 and are adjusted for inflation using the following correlation adopted from the Chemical Engineering Plant Cost Index (CEPCI)[56] (see eq 4)

$$\frac{\text{Cost}_{2021}}{\text{Cost}_{2014}} = \frac{\text{CEPCI}_{2021}}{\text{CEPCI}_{2014}} \quad (4)$$

where the values of CEPCI_{2014} and CEPCI_{2021} are, respectively, 576.1 and 655.9.[57] For this evaluation, the heat exchanger (evaporator, internal heat exchanger, and gas cooler) areas and compressor powers are needed and are obtained by simulations in Aspen Plus. An additional equipment cost is assumed to be 15% of the main purchased components in order to calculate the overall equipment cost of the heat pump.[58] The refrigerant cost is considered in the CAPEX calculation with the following prices: 0.5 \$/kg for CO_2, 0.72 \$/kg for CO_2/R41, and 1.2 \$/kg for CO_2/ethane.[59] Annualized capital costs are evaluated considering a life time for the process of 20 years, with an interest rate of 10%. A location factor is assumed for CAPEX, assuming that the plant is located in Switzerland. The updated location factor for 2021 is 0.58.[60]

3. RESULTS AND DISCUSSION

The thermodynamic model used in Aspen Plus is at first validated, simulating heat pump cycles for 1 kg of refrigerant with the main operating data reported in the literature (Wang et al.[49] for the CO_2/ethane mixture, Wang et al.[50] for the CO_2/R41 working fluid, Nekså et al.[33] for CO_2). As reported in the Supporting Information (Tables S1, S3, S5), good agreement is present between our simulations and literature research. The material and energy balances of the simulations reproducing the literature work are reported in Tables S2, S4, and S6 for Figures S1, S2, and S3, respectively.

3.1. Results of Sensitivity Analysis and KPI Evaluation. CO_2/ethane, CO_2/R41, and CO_2 amounts are found as described in Section 2.3 and are, respectively, 1750, 1454, and 1825 kg/h. A sensitivity analysis is conducted changing the compressor ratio, evaluating the water flow rate and COP for different supplied water temperatures. The results are reported in Figure 4 for the heat pump with the CO_2/ethane working fluid (Figure 4a is related to the water flow rate, while Figure 4b shows the COP, both changing the supplied water temperature and compressor ratio), in Figure 5 for the system with the CO_2/R41 mixture (Figure 5a,b shows the water flow rate and COP at different compressor ratios and outlet water temperatures, respectively), and in Figure 6 for the ASHP with the CO_2 refrigerant (Figure 6a shows the water flow rate, while Figure 6b shows the COP, both as a function of supplied water temperature and compressor ratio).

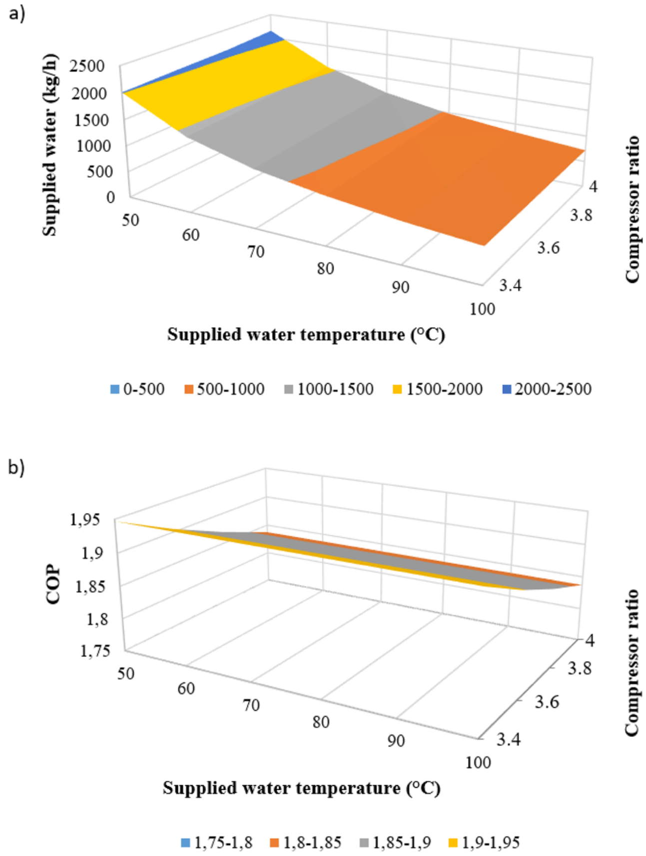


Figure 4. (a) Supplied water and (b) COP as a function of the supplied water temperature and compressor ratio for the ASHP with the CO_2/ethane working fluid.

The trend of the supplied water flow rate as a function of the compressor ratio and outlet water temperature is the same in Figures 4a, 5a, and 6a: the compressor ratio has a positive effect, while the supplied water temperature has a negative effect on the amount of water at the gas cooler. At a fixed compressor ratio, a lower amount of water is required to achieve a higher temperature up to 100 °C. At a fixed supplied water temperature, the flow rate of water increases with the compressor ratio because the discharge temperature of the refrigerant in the compressor is higher so that the refrigerant has a higher thermal load and a higher amount of water is required to maintain the same outlet water temperature.

On the other hand, the outlet water temperature is not significant for the COP, while the compressor ratio has a negative effect on it. At a fixed compressor ratio, the COP does not change with the outlet water temperature due to the same supplied thermal power and input electrical energy. At a fixed supplied water temperature, the COP decreases at a higher compressor ratio due to a more significant increase in electrical power.

https://doi.org/10.1021/acs.iecr.2c01816
Ind. Eng. Chem. Res. 2022, 61, 13221−13230

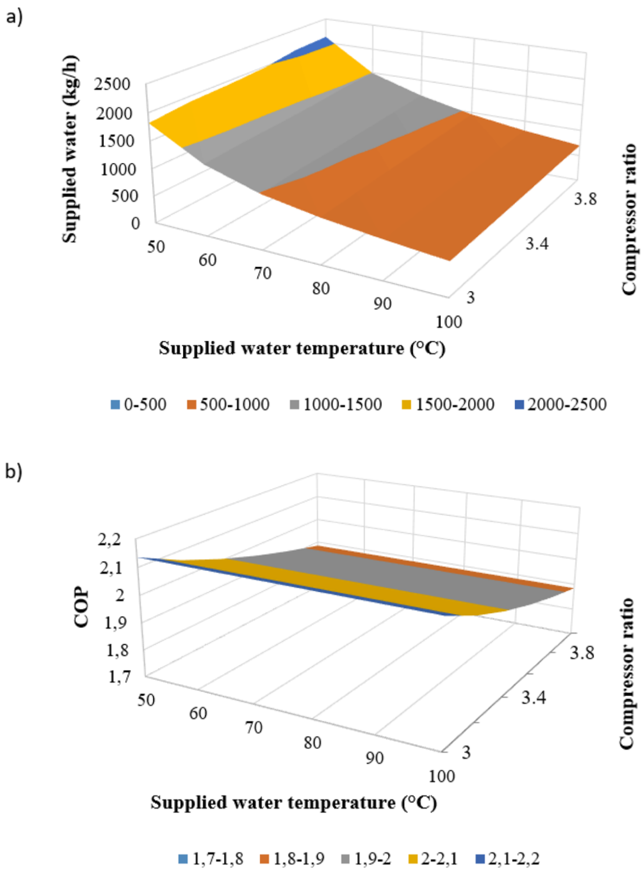


Figure 5. (a) Supplied water and (b) COP as a function of the supplied water temperature and compressor ratio for the ASHP with the CO_2/R41 working fluid.

For a supplied water temperature of 100 °C, as required for the regeneration of the adsorbent bed, data characterizing the integrated process are reported in Table 4, considering the lowest compressor ratio investigated in the sensitivity analysis in each case study in order to have the highest value of COP. In addition to the operating conditions, KPIs considering a grid electricity mix in Switzerland are shown.

From these results, it is evident that the best conditions are obtained using the CO_2/R41 working fluid: the COP value is 2.14 while ensuring a primary energy consumption, OPEX, and CO_2 emissions of 3.61 MJ/kW h, 0.062 $/kW h, and 0.08 kg/kW h, respectively. The system supplies 600 kg/h of water at 100 °C with a compressor ratio of 3. The worst conditions are when the mixture CO_2/ethane is used for the heat pump: the COP has the lowest value of 1.95, while the KPIs have the highest values (3.85 MJ/kWh, 0.066 $/kW h, and 0.088 kg/kW h, respectively, for the primary energy consumption, OPEX, and CO_2 emissions).

For all investigated heat pumps providing hot water at 100 °C, the COP value is around 2, suggesting a good efficiency after a comparison with the literature research. In fact, other ASHPs using other refrigerants and other cycles have a COP of about 2 for a lower supplied water temperature (50−75 °C).[61−66] On the other hand, the COP value is in agreement with other trans-critical ASHPs using CO_2, for which a slightly higher COP is obtained for a slightly lower supplied water temperature.[15,19,67]

3.2. Results of Energy Consumption. An analysis of the energy consumption is conducted considering the heat pumps

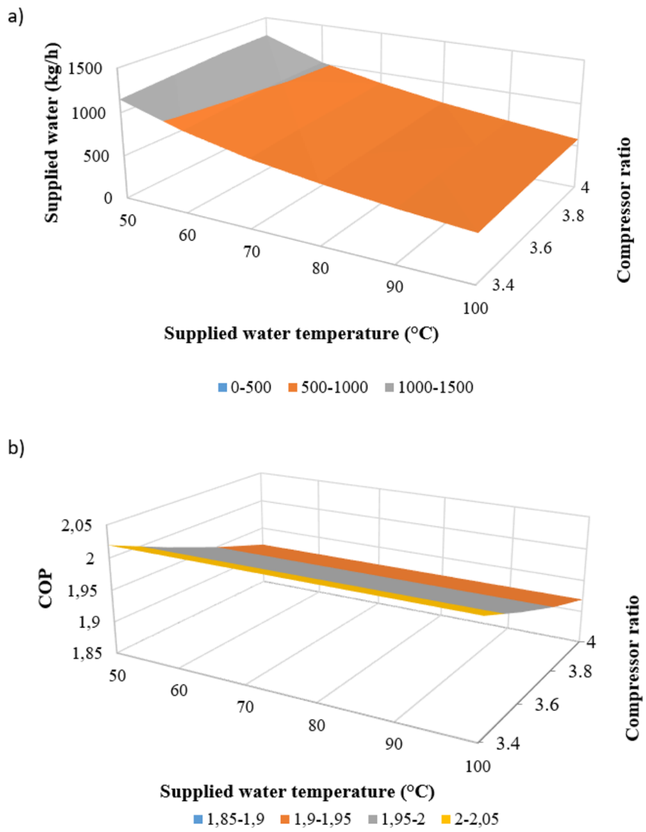


Figure 6. (a) Supplied water and (b) COP as a function of the supplied water temperature and compressor ratio for the ASHP with the CO_2 working fluid.

Table 4. Operating Conditions and KPIs of ASHPs Integrated into the DAC Adsorption System

operating conditions			
working fluid	CO_2	CO_2-R41	CO_2-ethane
ambient air temperature (°C)	25	25	25
inlet water temperature (°C)	8	25	25
water supplied temperature (°C)	100	100	100
supplied water (kg/h)	528	600	660
compressor ratio	3.4	3	3.4
COP	2.02	2.14	1.95
Key Performance Indicators			
primary energy consumption (MJ/kW h)	3.71	3.51	3.85
OPEX ($/kW h)	0.064	0.062	0.066
CO_2 emissions (kg/kW h)	0.085	0.080	0.088

designed to supply hot water at 100 °C with the lowest investigated compressor ratio. A heat exchanger is used to simulate in Aspen Plus the desorption and cooling stages. In the first case, it is set up that the hot water rejects heat up to achieving a temperature of 25 °C (the outlet water temperature is fixed at 25 °C), allowing to find the total amount of the released thermal load. In the second case, the amount of heat to be removed (i.e., the same required for the desorption stage) is defined in the heat exchanger of the simulation in Aspen Plus, finding the outlet air temperature. The DAC adsorption process requires 1427 kWh/tonCO_2 of heat for regeneration: compared to the DAC using an MWI, a surplus of heat is present in all integrated and investigated systems as reported in Table 5.

https://doi.org/10.1021/acs.iecr.2c01816
Ind. Eng. Chem. Res. 2022, 61, 13221−13230

Table 5. Energy Consumption Analysis for the Regeneration and Cooling Stages

working fluid	CO_2	CO_2-R41	CO_2-ethane
Regeneration Stage			
heat released by ASHP (kW h/tonCO_2)	9766	9061	9946
required heat (kW h/tonCO_2)	1427	1427	1427
surplus of heat (kW h/tonCO_2)	8339	7634	8519
Cooling Stage			
outlet air temperature (°C)	17	18	18
cooling duty (kW h/tonCO_2)	1427	1427	1427

The heat pump using CO_2-ethane ensures the highest surplus of heat (8519 kWh/tonCO_2), while the cold air is heated up to 18 °C in the cooling stage. The amount of heat that is not used could be used in a dryer to remove water in the air before the adsorption stage, improving the energy efficiency of the overall system and underlining the advantage of using an ASHP instead of an MWI.

Moreover, the energy consumption of the integrated system is lower than that of the single DAC adsorption process with an MWI and a cooling tower. Table 6 shows the total energy use for the single DAC, requiring 1427 kWh/tonCO_2 of thermal energy. To satisfy this amount of heat and simultaneously the required electricity, 1142 kg of wastes is required by the incinerator (4.5 MJ of thermal energy per kg of waste is produced).[68] The MWI needs heat and electricity to work, respectively, 0.24 MJ per kg of waste and 0.36 MJ per kg of waste.[68] Considering the amount of captured CO_2 and required wastes, 76 kWh/tonCO_2 of thermal energy and 114 kWh/tonCO_2 of electrical energy are necessary for the MWI. In addition to this energy consumption, 11251 kWh/tonCO_2 of electrical energy is needed for the cooling tower (with a capacity of 9 kW) used for the cooling stage of the adsorbent bed.[69] Considering the MWI and cooling tower, the single adsorption process requires 11441 kWh/tonCO_2 of energy.

Table 6. Overall Energy Consumption of the Base Case DAC Adsorption Process

heat for regeneration	1427	kW h/tonCO_2
produced heat from waste	4.5	MJ/kg_{waste}
required waste for heat production	1142	kg_{waste}/tonCO_2
input heat for MWI	0.24	MJ/kg_{waste}
input heat	274	MJ/tonCO_2
captured CO_2	0.0067	tonCO_2/h
input heat for MWI	76	kW h/tonCO_2
input electricity for MWI	0.36	MJ/kg_{waste}
input electricity for MWI	411	MJ/tonCO_2
input electricity for MWI	114	kW h/tonCO_2
cooling tower capacity	9	kW
input electricity for the cooling tower	11251	kW h/tonCO_2
overall energy for DAC	11441	kW h/tonCO_2

This value is higher than the energy consumption of the system integrating an ASHP and a DAC adsorbent bed (which also does not require any water). The key input is just electrical energy for the compressor of the heat pump and fans of DAC. In particular, 4835, 4239, and 5109 kWh/tonCO_2 are required for the ASHP using, respectively, CO_2, CO_2/R41, and CO_2/ethane. 284 kWh/tonCO_2 is needed for fans, and the overall energy consumptions related to the CO_2, CO_2/R41, and CO_2/ethane systems are, respectively, 5118, 4521, and 5391 kWh/tonCO_2. Compared to the base case scheme, savings in energy consumption of 55, 60, and 53% are achieved for the integrated processes using CO_2, CO_2/R41, and CO_2/ethane, respectively, as the refrigerants in the heat pump.

3.3. Results of Economic Analysis. An economic analysis is carried out with the evaluation of CAPEX and OPEX for each process with the heat pump providing hot water at 100 °C at the lowest investigated compressor ratio. Table S7 shows the CAPEX calculation of the integrated system using different refrigerants.

Tables S8−S10 of the Supporting Information report the purchase cost for the equipment of each heat pump. The heat pump using CO_2 costs 92200 \$, while the heat pumps using CO_2/R41 and CO_2/ethane cost, respectively, 79600 \$ and 91000 \$. Locating the system in Switzerland, the ASHP using CO_2, CO_2/R41, and CO_2/ethane costs, respectively, 53900 \$, 46600 \$, and 53200 \$, which, considering the supplied thermal power and the working fluid cost, corresponds to 830, 773, and 806 \$/kW h, respectively. These specific costs are in agreement with those reported in Popovski et al.[70] for an ASHP. For the refrigerant volume estimation, a cycle time of 0.1 h is assumed, as are 175 kg of CO_2/ethane, 145 of CO_2/R41, and 183 kg of CO_2.[71] The purchase costs for the adsorbent bed and fan are the same as those reported in Leonzio et al.[44] Locating the plant in Switzerland, the results show that the specific levelized CAPEX of the overall integrated process using CO_2, CO_2/R41, and CO_2/ethane is 787, 709, and 781 \$/tonCO_2, respectively.

Table S11 shows the OPEX calculation when the electricity grid is used as the source in the DAC and heat pump systems. For the electricity grid, 0.11 \$/kW h is assumed.[72] The operating costs of the overall process are 2160, 1940, and 2180 \$/tonCO_2 when CO_2, CO_2/R41, and CO_2/ethane are, respectively, used in the heat pump.

In this way, the total cost of the integrated process using CO_2 is 2950 \$/tonCO_2, while the process using CO_2/R41 and CO_2/ethane costs totally 2650 and 2960 \$/tonCO_2, respectively. These total costs are higher than that of the single DAC adsorption system of 751 \$/tonCO_2.

However, the use of ASHPs may be supported by economic incentives provided by the government and related to the supplied power.[73] This program aims at increasing the use of renewable energy and improving the energy efficiency. The selected value of subsides has the same order of magnitude of current economic incentives used in other countries (0.15 \$/kW h in the UK).[74]

A sensitivity analysis is conducted changing the electricity source (hydro energy, wind energy, *PV* panel, geothermal energy, *PV/T* system, and grid system) to evaluate the total cost of the new proposed process. The cost of electricity in Switzerland from hydro energy is 0.078 \$/kW h, that from wind energy is 0.12 \$/kW h, that from *PV* is 0.1 \$/kW h, that from geothermal energy is 0.18 \$/kW h, and that from *PVT* is 0.067 \$/kW h.[72]

The value of the economic incentives is in the range between 0.05 and 0.25 \$/kW h. The results are reported in Table 7: only for higher levels of incentives, economic benefits are ensured with a net total cost lower than that of the base case. Moreover, the use of a *PV/T* solar panel for electricity production guarantees the lowest net total cost for the integrated system, taking into account 0.25 \$/kW h for economic subsidies. In particular, by using the CO_2-R41 refrigerant, the lowest net total cost is present (39 \$/tonCO_2).

The use of this refrigerant is the best and convenient from an economic and energetic point of view: the lowest total cost

https://doi.org/10.1021/acs.iecr.2c01816
Ind. Eng. Chem. Res. 2022, 61, 13221−13230

Table 7. Net Total Cost of the Integrated Processes at Different Sources of Electrical Energy

			refrigerant		
			CO_2	CO_2-R41	CO_2-ethane
electricity source	electricity price ($/kW h)	economic incentives for ASHP ($/kW h)	net total cost ($/ton$CO_2$)		
grid mix	0.11	0.05	2430	2170	2440
		0.1	1920	1690	1910
		0.2	886	735	863
		0.25	371	257	338
hydro	0.078	0.05	2250	2010	2240
		0.1	1730	1530	1720
		0.2	702	573	670
		0.25	187	95	145
wind	0.12	0.05	2490	2220	2500
		0.1	1970	1740	1970
		0.2	943	786	924
		0.25	428	308	399
PV	0.1	0.05	2370	2120	2380
		0.1	1860	1640	1850
		0.2	828	684	803
		0.25	313	207	278
geothermal	0.18	0.05	2830	2520	2860
		0.1	2320	2050	2340
		0.2	1288	1090	1287
		0.25	773	613	762
PVT	0.067	0.05	2180	1950	2180
		0.1	1670	1470	1650
		0.2	639	517	603
		0.25	124	39	78

with economic incentives and the highest energy saving compared to the base case scenario are obtained. We note that the costs established here are for current technologies and anticipate significant cost reductions through scale-up and learning in both the industrial ASHP and the DAC systems as well as reductions in the cost of renewable electricity.

4. CONCLUSIONS

DAC adsorption is an emerging technology that requires large air flow rates and energy consumption that could be provided by an ASHP. For this reason, a new process integrating an ASHP and a DAC adsorption system is proposed in this research work.

In this scheme, three separate stages (adsorption, cooling, and regeneration) of the adsorption technology are considered. The air is sent to the adsorbent bed at first and after that to the evaporator of the heat pump, and then it is used for the cooling stage. Simultaneously, the heat pump supplies hot water at 100 °C that can be used for the regeneration of the DAC. This level of temperature is required for the desorption; hence, water temperatures higher than those proposed in the literature are here suggested for an ASHP. Moreover, this kind of integration has not been investigated in the literature so far, and a comparison with a scheme proposed by Climeworks company is presented. In the considered conventional DAC scheme, thermal and electrical energies are provided by an MWI and cooling by a cooling tower.

For the heat pump, three different working fluids, including CO_2/ethane, CO_2/R41, and CO_2, are investigated in a trans-critical cycle.

The results show that ASHPs supplying hot water at 100 °C have good efficiencies in terms of COP. Economic (if economic incentives are provided) and energetic advantages may be present in the proposed and integrated scheme compared to the traditional one.

An energetic analysis is conducted finding that the overall energy consumption of the integrated process using CO_2, CO_2/R41, and CO_2/ethane is, respectively, 5118, 4521, and 5391 kW h/tonCO_2. Electrical energy is required for fans and the compressor of the heat pump. Compared to the base case process, savings in energy consumption of 55, 60, and 53% are possible for the integrated processes using CO_2, CO_2/R41, and CO_2/ethane, respectively, in the ASHP.

From an economic analysis, it is found that a net total cost lower than that of the conventional process (751 $/ton$CO_2$) is ensured in the proposed system if an opportune financial subsidy is provided. By analyzing several electricity sources, lower total costs are present when a *PV/T* solar panel is used for the electrical energy generation. In particular, the lowest net total cost (39 $/ton$CO_2$) is present if CO_2/R41 is used in the heat pump and if 0.25 $/kW h of incentives is given by the government.

The best economic and energetic performances are provided by using CO_2/R41 in the ASHP integrated into the DAC adsorption system. We also expect steep cost reductions in both the ASHP and DAC capital costs. Overall, the proposed integrated scheme could be used when no heat source is present, ensuring at the same time a negative value for the climate change as for the basic process.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c01816.

Validation of the simulation models and cost analysis of ASHPs (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Grazia Leonzio − *Department of Chemical Engineering, Imperial College London, London SW7 2AZ, U.K.;* orcid.org/0000-0002-6460-3519; Email: g.leonzio20@imperial.ac.uk

Author

Nilay Shah − *Department of Chemical Engineering, Imperial College London, London SW7 2AZ, U.K.*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.2c01816

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was made possible by funding from the Hadley Trust, which is gratefully acknowledged.

■ REFERENCES

(1) Our World in Data. 2021, available at: https://ourworldindata.org/energy-production-consumption#how-is-global-energy-consumption-changing-year-to-year accessed on (Aug 8, 2021).

(2) IEA. 2020, available at: https://www.iea.org/data-and-statistics/?country=WORLD&fuel=CO2%20emissions&indicator=TotCO2 accessed on (Aug 8, 2021).

(3) Li, Y.; Zhang, N.; Ding, Z. Investigation on the energy performance of using air-source heat pump tocharge PCM storage tank. *J. Energy Storage* **2020**, *28*, 101270.

(4) Deng, J.; Wang, R. Z.; Han, G. Y. A review of thermally activated cooling technologies for combined cooling, heating and power systems. *Prog. Energy Combust. Sci.* **2011**, *37*, 172−203.

(5) Sun, S.; Guo, H.; Lu, D.; Bai, Y.; Gong, M. Performance of a single-stage recuperative high-temperature air source heat pump. *Appl. Therm. Eng.* **2021**, *193*, 116969.

(6) IEA Heat Pump Centre. How Heat pumps can help address today's key energy policy concerns. 2005, available at: http://www.heatpumpcentre.org/ (accessed on Aug 8, 2021).

(7) Carroll, P.; Chesser, M.; Lyons, P. Air Source Heat Pumps field studies: a systematic literature review. *Renewable Sustainable Energy Rev.* **2020**, *134*, 110275.

(8) Song, M.; Chaobin, D.; Ning, M.; Shiming. Energy transfer procession in an air source heat pump unit during defrosting with melted frost locally drainage in its multi-circuit outdoor coil. *Appl. Energy* **2018**, *164*, 109.

(9) Wu, Y.; Wang, W.; Sun, Y. Y.; Cui, Y. M.; Duan, D. X.; Deng, S. M. An equivalent temperature drop method for evaluating the operating performances of ASHP units jointly affected by ambient air temperature and relative humidity. *Energy Build.* **2018**, *224*, 110211.

(10) Ozturk, M. M.; Dogan, B.; Erbay, L. B. Performance assessment of an air source heat pump water heater from exergy aspect. *Sustainable Energy Technol. Assess.* **2020**, *42*, 100809.

(11) IEA. 2021, available at: https://www.iea.org/reports/heat-pumps (accessed on Aug 2, 2021).

(12) Minglu, Q.; Yanan, F.; Jianbo, C.; Tianrui, L.; Zhao, L.; He, L. Experimental study of a control strategy for a cascade air source heat pump water heater. *Appl. Therm. Eng.* **2017**, *110*, 835−843.

(13) Hu, B.; Wang, R. Z.; Xiao, B.; He, L.; Zhang, W.; Zhang, S. Performance evaluation of different heating terminals used in air source heat pump system. *Int. J. Refrig.* **2019**, *98*, 274−282.

(14) Xu, L.; Li, E.; Xu, Y.; Mao, N.; Shen, X.; Wang, X. An experimental energy performance investigation and economic analysis on a cascade heat pump for high-temperature water in cold region. *Renewable Energy* **2020**, *152*, 674−683.

(15) Dai, B.; Qi, H.; Dou, W.; Liu, S.; Zhong, D.; Yang, H.; Nian, V.; Hao, G. Life cycle energy, emissions and cost evaluation of CO2 air source heat pump system to replace traditional heating methods for residential heating in China: System configurations. *Energy Convers. Manage.* **2020**, *218*, 112954.

(16) Guo, H.; Gong, M. Q.; Qin, X. Y. Performance analysis of a modified subcritical zeotropic mixture recuperative high-temperature heat pump. *Appl. Energy* **2019**, *237*, 338−352.

(17) Wu, J.; Yang, Z.; Wu, Q.; Zhu, Y. Transient behavior and dynamic performance of cascade heat pump water heater with thermal storage system. *Appl. Energy* **2012**, *91*, 187−196.

(18) Zhang, F.; Cai, J.; Ji, J.; Han, K.; Ke, W. Experimental investigation on the heating and cooling performance of a solar air composite heat source heat pump. *Renewable Energy* **2020**, *161*, 221−229.

(19) Fernandez, N.; Hwang, Y.; Radermacher, R. Comparison of CO2 heat pump water heater performance with baseline cycle and two high COP cycles. *Int. J. Refrig.* **2010**, *33*, 635−644.

(20) Lorentzen, G.; Pettersen, J. A new, efficient and environmentally benign system for car air-conditioning. *Int. J. Refrig.* **1993**, *16*, 4−12.

(21) Hu, B.; Li, Y.; Wang, R. Z.; Cao, F.; Xing, Z. Real-time minimization of power consumption for air-source transcritical CO 2 heat pump water heater system. *Int. J. Refrig.* **2018**, *85*, 395−408.

(22) Wang, S.; He, Y.; Tuo, H.; Cao, F.; Xing, Z. Effect of heat transfer area and refrigerant mass flux in a gas cooler on heating performance of air-source transcritical CO2 heat pump water heater system. *Energy Build.* **2013**, *67*, 1−10.

(23) Boccardi, G.; Botticella, F.; Lillo, G.; Mastrullo, R.; Mauro, A. W.; Trinchieri, R. Experimental investigation on the performance of a transcritical CO 2 heat pump with multi-ejector expansion system. *Int. J. Refrig.* **2017**, *82*, 389−400.

(24) Liao, S. M.; Zhao, T. S.; Jakobsen, A. A correlation of optimal heat rejection pressures in transcritical carbon dioxide cycles. *Appl. Therm. Eng.* **2000**, *20*, 831−841.

(25) Saikawa, M.; Koyama, S. Thermodynamic analysis of vapor compression heat pump cycle for tap water heating and development of CO 2 heat pump water heater for residential use. *Appl. Therm. Eng.* **2016**, *106*, 1236−1243.

(26) Fernandez, N.; Yunho, H.; Reinhard, R. Comparison of CO2 heat pump water heater performance with baseline cycle and two high COP cycles. *Int. J. Refrig.* **2010**, *33*, 635−644.

(27) Song, Y.; Cao, F. The evaluation of the optimal medium temperature in a space heating used transcritical air-source CO2 heat pump with an R134a subcooling device. *Energy Convers. Manage.* **2018**, *166*, 409−423.

(28) Lu, F.; Liu, S.; Dai, B.; Zhong, Z.; Li, H.; Sun, Z. Experimental Study on Thermal Performance of Transcritical CO2 Air Source Heat Pump for Space Heating. *Energy Procedia* **2019**, *158*, 5913−5919.

(29) Laipradit, P.; Tiansuwan, J.; Kiatsiriroat, T.; et al. Theoretical performance analysis of heat pump water heaters using carbon dioxide as refrigerant. *Int. J. Energy Res.* **2008**, *32*, 356−366.

(30) Nekså, P. CO2 heat pump systems. *Int. J. Refrig.* **2002**, *25*, 421−427.

(31) Anstett, P. *Measurement of the Performance of an Air/Water Heat Pump Using CO_2 or R744 for the Production of Hot Water for Use in a Hospital*; IEA Heat Pump Centre Newsl, 2006; pp 35−38.

(32) Minetto, S. Theoretical and experimental analysis of a CO2 heat pump for domestic hot water. *Int. J. Refrig.* **2011**, *34*, 742−751.

(33) Nekså, P.; Rekstad, H.; Zakeri, G. R.; Schiefloe, P. A. CO2-heat pump water heater: characteristics, system design and experimental results. *Int. J. Refrig.* **1998**, *21*, 172−179.

(34) Zhu, Y. H.; Huang, Y. L.; Li, C. H.; Zhang, F. Z.; Jiang, P. X. Experimental investigation on the performance of transcritical CO2 ejector-expansion heat pump water heater system. *Energy Convers. Manage.* **2018**, *167*, 147−155.

(35) Yu, J.; Xu, Z.; Tian, G. A thermodynamic analysis of a transcritical cycle with refrigerant mixture R32/R290 for a small heat pump water heater. *Energy Build.* **2010**, *42*, 2431−2436.

(36) Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Direct Capture of CO2 from Ambient Air. *Chem. Rev.* **2016**, *116*, 11840−11876.

(37) Shi, X.; Xiao, H.; Azarabadi, H.; Song, J.; Wu, X.; Chen, X.; Lackner, K. S. Sorbents for the Direct Capture of CO 2 from Ambient Air. *Angew. Chem., Int. Ed.* **2020**, *59*, 6984−7006.

(38) Sabatino, F.; Mehta, M.; Grimm, A.; Gazzani, M.; Gallucci, F.; Kramer, G. J.; van Sint Annaland, M. Evaluation of a Direct Air Capture Process Combining Wet Scrubbing and Bipolar Membrane Electrodialysis. *Ind. Eng. Chem. Res.* **2020**, *59*, 7007−7020.

(39) Eisaman, M. D.; Schwartz, D. E.; Amic, S.; Larner, D. L.; Zesch, J.; Torres, F.; Littau, K. Energy-Efficient Electrochemical CO2 Capture from the Atmosphere. *Technical Proceedings of the 2009 Clean Technology Conference and Trade Show, Houston, TX, May 3−7,* 2009.

(40) Kelemen, P. B.; McQueen, N.; Wilcox, J.; Renforth, P.; Dipple, G.; Vankeuren, A. P. Engineered carbon mineralization in ultramafic rocks for CO2 removal from air: Review and new insights. *Chem. Geol.* **2020**, *550*, 119628.

(41) von Hippel, T. Thermal Removal of Carbon Dioxide from the Atmosphere: Energy Requirements and Scaling Issues. *Clim. Change* **2018**, *148*, 491.

(42) Adamu, A.; Russo-Abegão, F.; Boodhoo, K. Process intensification technologies for CO2 capture and conversion—a review. *Chem. Eng* **2020**, *2*, 2.
(43) Fasihi, M.; Efimova, O.; Breyer, C. Techno-economic assessment of CO2 direct air capture plants. *J. Cleaner Prod.* **2019**, *224*, 957−980.
(44) Leonzio, G.; Fennell, P. S.; Shah, S. A comparative study of different sorbents in the context of direct air capture (DAC): evaluation of key performance indicators and comparisons. *Appl. Sci.* **2022**, *12*, 2618.
(45) Sánchez, D.; Patiño, J.; Llopis, R.; et al. New positions for an internal heat exchanger in a CO2 supercritical refrigeration plant. Experimental analysis and energetic evaluation. *Appl. Therm. Eng.* **2014**, *63*, 129−139.
(46) Jin, W.; Liming, T.; Haiming, Q. I.; Qi, C.; Guangming, C. Effect of mixing chamber diameter on performance of transcritical CO2 heat pump system with ejector. *CIESC J.* **2016**, *67*, 1719−1724.
(47) Lee, H. S.; Kim, H. J.; Jung, D. A novel working fluid for building air-conditioning and ocean thermal energy conversion. *Korean J. Chem. Eng.* **2014**, *31*, 1732−1735.
(48) Wang, D.; Liu, Y.; Kou, Z.; Yao, L.; Lu, Y.; Tao, L.; Xia, P. Energy and exergy analysis of an air-source heat pump water heater system using CO2/R170 mixture as an azeotropy refrigerant for sustainable development. *Int. J. Refrig.* **2019**, *106*, 628−638.
(49) Wang, D.; Chen, Z.; Gu, Z.; Liu, Y.; Kou, Z.; Tao, L. Performance analysis and comprehensive comparison between CO2 and CO2/ethane azeotropy mixture as a refrigerant used in single-stage and two-stage vapor compression transcritical cycles. *Int. J. Refrig.* **2020**, *115*, 39−47.
(50) Wang, D.; Lu, Y.; Tao, L. Thermodynamic analysis of CO2 blends with R41 as an azeotropy refrigerant applied in small refrigerated cabinet and heat pump water heater. *Appl. Therm. Eng.* **2017**, *125*, 1490−1500.
(51) Climeworks. 2020, available at www.climeworks.com (accessed on July, 2020).
(52) VITO. *Training Event-Carbon Capture, Utilization and Storage (CCUS), AvansHogeschool*; VITO: Breda, Netherlands, 2020.
(53) Øi, L. E.; Tirados, I. Y. Heat Pump Efficiencies simulated in Aspen HYSYS and Aspen Plus. *Proceedings of the 56th SIMS October 07-09 2015, Linköping, Sweden*, 2015.
(54) Peter, M. S.; Timmerhaus, K. D. *Plant Design and Economics for Chemical Engineering*; McGraw-Hill, 1991.
(55) Matches. 2021, available at: http://www.matche.com/equipcost/Default.html (accessed on Nov, 2020).
(56) Wijesiri, R. P.; Knowles, G. P.; Yeasmin, H.; Hoadley, A. F. A.; Chaffee, A. L. Technoeconomic Evaluation of a Process Capturing CO2 Directly from Air. *Processes* **2019**, *7*, 503.
(57) TowerlingSkills. 2021, available at: https://www.toweringskills.com/financial-analysis/cost-indices/ (accessed on Aug 5, 2021).
(58) Wang, Y.; Ye, Z.; Song, Y.; Yin, X.; Cao, F. Energy, economic and environmental assessment of transcritical carbon dioxide heat pump water heater in a typical Chinese city considering the defrosting. *Energy Convers. Manage.* **2021**, *233*, 113920.
(59) Alibaba. 2021, available at https://www.alibaba.com.
(60) Perry, R. H. *Perry's Chemical Engineerings' Handbook*; McGraw-Hill, 1999.
(61) Wang, Y.; You, S.; Sun, Y.; Li, Z. Experimental investigations and operational performance analysis on an air source heat pump unit for domestic hot water supply in South China. *Procedia Eng.* **2017**, *205*, 2407−2414.
(62) Zhijiang, W.; Jinping, L.; Xuewei, Z. Experimental Investigation on High-temperature Heat Pump Water Heater of R1234ze. *Proceedings of the 5th International Conference on Advanced Design and Manufacturing Engineering*; Atlantis Press, 2015; pp 1403−1406.
(63) Xu, Y.; Huang, Y.; Jiang, N.; Song, M.; Xie, X.; Xu, X. Experimental and theoretical study on an air-source heat pump water heater for northern China in cold winter: Effects of environment temperature and switch of operating modes. *Energy Build.* **2019**, *191*, 164−173.
(64) Ibrahim, O.; Fardoun, F.; Younes, R.; Louahlia-Gualous, H. Air source heat pump water heater: Dynamic modeling, optimal energy management and mini-tubes condensers. *Energy* **2014**, *64*, 1102−1116.
(65) Chen, X.; Liu, C.; Yang, J.; Chen, J. Experimental study on R-22, R-427A, R-161 and R-290 in air-source heat pump for space heating at low ambient temperatures. *Int. J. Refrig.* **2018**, *96*, 147−154.
(66) Chaiwongsa, P.; Duangthongsuk, W. Hot Water Making Potential Using of a Conventional Air-Conditioner as an Air-Water Heat Pump. *Procedia Eng.* **2011**, *8*, 165−170.
(67) Wang, S.; Tuo, H.; Cao, F.; Xing, Z. Experimental investigation on air-source transcritical CO2 heat pump water heater system at a fixed water inlet temperature. *Int. J. Refrig.* **2013**, *36*, 701−716.
(68) Hellweg, S.; Hofstetter, T. B.; Hungerbühler, K. Modeling waste incineration for life-cycle inventory analysis in Switzerland. *Environ. Model. Assess.* **2001**, *6*, 219−235.
(69) Atlas. 2021, available at: https://www.evapco.eu/sites/evapco.eu/files/2020-12/EVAPCO%20AT%20Atlas%20Bulletin-E_0820.pdf (accessed on July 7, 2021).
(70) Popovski, E.; Fleiter, T.; Santos, H.; Leal, V.; Fernandes, E. O. Technical and economic feasibility of sustainable heating and cooling supply options in southern European municipalities-A case study for Matosinhos, Portugal. *Energy* **2018**, *153*, 311−323.
(71) Green, R. *The Effects of Cycling on Heat Pump Performance*; Department of Energy and Climate Change (DECC), Report, 2012.
(72) Bauer, C.; Hirschberg, S.; Bäuerle, Y.; Biollaz, S.; CalbryMuzyka, A.; Cox, B.; Heck, T.; Lehnert, M.; Meier, A.; Prasser, M. H.; Schenler, W.; Treyer, K.; Vogel, F.; Wieckert, H. C.; Zhang, X.; Zimmermann, M.; Burg, V.; Bowman, G.; Erni, M.; Saar, M.; Tran, M. Q. Potentials, costs and environmental assessment of electricity generation technologies. 2017, available at: https://www.psi.ch/sites/default/files/import/lea/HomeEN/Final-Report-BFE-Project.pdf (accessed on May 5, 2021).
(73) Kiss, B.; Neij, L.; Jakob, M. *Heat Pumps: A Comparative Assessment of Innovation and Diffusion Policies in Sweden and Switzerland. Historical Case Studies of Energy Technology Innovation in: Chapter 24, the Global Energy Assessment*; Grubler, A., Aguayo, F., Gallagher, K. S., Hekkert, M., Jiang, K., Mytelka, L., Neij, L., Nemet, G., Wilson, C., Eds.; Cambridge University Press: Cambridge, U.K., 2012.
(74) Wang, Y.; He, W. Temporospatial techno-economic analysis of heat pumpsfor decarbonising heating in Great Britain. *Energy Build.* **2021**, *250*, 111198.

https://doi.org/10.1021/acs.iecr.2c01816
Ind. Eng. Chem. Res. 2022, 61, 13221−13230