CONTENT

Birol Kılkış

A Second-law Model for the Decarbonization Potential of Heat Pumps

OSTIM Technical University, Ankara, Türkiye

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Abstract

Based solely on the First Law of Thermodynamics, which addresses energy efficiency, heat pumps are considered to be a major asset for achieving the decarbonization goals of the Paris Agreement. Yet, this approach alone overestimates the potential for decarbonization and conceals certain root causes of carbon dioxide emissions arising from exergy destruction. This paper redefines the decarbonization potential of heat pumps holistically by applying the First and Second Laws of thermodynamics together. This research shows that power-to-heat energy conversion systems are responsible for exergy destruction, leading to additional carbon dioxide emissions, as the destroyed exergy must be offset by other means, possibly by burning fossil fuels. An exergy-based model was developed and used for different scenarios. Results were compared with boilers in heating mode fueled by fossil fuels or biogas, and with adsorption machines in cooling mode. Thermal energy storage systems and their optimal operational regimes for minimum environmental footprint have also been considered and modeled in accordance with the Second Law of Thermodynamics. A correction factor for the coefficient of performance of heat pumps has been developed to account for exergy destruction and emission avoidance associated with typical heat pump operation under electrical and ambient thermal inputs. Results show that today's coefficient of performance must be higher to meet the emissions-mitigation and total electrification targets to mitigate global warming. The Second Law of thermodynamics shows that the case study about the comfort cooling system of a nature center building with ground source heat pumps and photovoltaic panels is responsible for emissions by 0.81 kg CO_2 emissions/kW$_{en}$-h, rather than saving 1.62 kg CO_2/kWen-h by a no-heat pump case, comprising solar photovoltaic panels, adsorption cooling, and desiccant wheel. This case study also shows that the carbon dioxide emission responsibility resulting from exergy destruction during the power-to-heat process is as important as the direct emissions from electric power use. This paper concludes that the exergy destruction-related carbon footprint should not be neglected across all design and application phases to foster better awareness and establish exergy-rational strategy planning towards the Paris Agreement goals.

Keywords: *Heat pumps; Rational Exergy Management Model; Exergy destructions; Near-zero building; Avoidable CO2 emissions responsibility*

1. Introduction

According to the European Commission (EC), heat pumps are expected to play a key role in the clean energy transition and to help achieve the European Union's (EU) goal of carbon neutrality by 2050 [1]. Europe's heating and cooling energy demand accounts for almost 50% of total gross final energy consumption [2]. To meet demand, the contribution of renewable energy sources, including biomass and heat pumps, is increasing [3]. In this respect, `green electricity-driven` heat pumps are considered to have a key role. These studies all depend on the First Law, which addresses only the quantity of energy and energy efficiency. On the other hand, even if electricity is generated entirely from green energy sources like solar photovoltaic panels, the panels operate at a modest First-Law efficiency, and the remaining exergy (quality) of the solar energy input is wasted (destroyed). The destroyed thermal exergy must be offset by another energy conversion system, like a boiler, which may use fossil fuels. The carbon dioxide emissions from the boiler are, in fact, the responsibility of the solar PV system. Furthermore, the boiler does not generate electric power upstream of thermal energy generation. This is another example of exergy destruction and carbon dioxide emission responsibility in a diminishing return series [4]. Another example is thermal power plants, where waste heat downstream of power generation is wasted in cooling towers, unless it is utilized in district energy systems [5]. These examples show that current energy-efficiency and carbon-footprint analyses are necessary but not sufficient, lacking the additional insights yet to be provided by the Second Law. Despite this, Thomaßen and others conducted parametric studies on the effectiveness of heat pumps in decarbonizing the heating sector in Europe using the First Law [6]. They stated that the existing power sector can accommodate 1.1-1.6 TW_H of heat pumpsFirst Law.

TU Delft participated in a project called Dezonnet in the Netherlands, which uses low-temperature solar heat with heat pumps in a small district of Haarlem [7]. The small grid also includes a large underground aquifer-type thermal energy storage (TES) system. Their report claims a large emission-reduction potential from eliminating the use of fossil fuels. However, they did not consider exergy destruction due to power-to-heat conversion by the heat pumps, the small exergy destruction in the solar PVT panels, or exergy destruction attributable to the TES system.

Heat pumps consume electric power, which has a high unit exergy of 0.95 kW_{ex}/kW_{en}, whereas, based on the ideal Carnot cycle, the unit exergy of thermal power is in the range of 0.03 kW_{ex}/kW_{en} in low-temperature heating, 0.02 kW_{ex}/kW_{en} in cooling, including latent loads (dehumidification), and 0.15 kW_{ex}/kW_{en} for domestic hot water (DHW). The large unit exergy mismatch between the electricity used and the thermal energy produced calls for a higher coefficient of performance (*COP*) to offset the exergy destruction. For example, the ideal *COP* for indoor space heating in a regime of a supply temperature of 330 K and a return temperature of 310 K is around 5, according to the ideal Carnot cycle, to match the supply and demand exergy. Otherwise, the exergy mismatch translates into ΔCO_2because the high unit exergy of electric power is grossly destroyed (wasted). This requires recognizing the second law of thermodynamics to assess the environmental impact of heat pumps accurately.

The contribution of a heat pump to CO_2 mitigation may have two aspects. First, a heat pump, which uses renewable energy sources and systems, replaces a boiler that consumes fossil fuels, with a performance coefficient greater than 1. Second, heat pumps can introduce low-enthalpy waste heat and ambient heat (or sink-in cooling) into the energy sector by better matching resource temperatures to demand temperatures. However, a heat pump uses electricity, which has a high unit exergy regardless of how it is generated or from which energy source. The thermal exergy (heat or cold) has a much lower unit exergy. Therefore, the mismatch is responsible for ΔCO_2, and irreversible exergy destruction results.

The objective of this work is to provide sufficient awareness of the ΔCO_2 term, thereby revealing sustainable, more effective measures against global warming by recognizing the direct relationship between exergy destruction and ΔCO_2. The carbon dioxide concentration is measured in the atmosphere, but a major part of the root causes on the ground remain unknown.

2. Development of the Model

To address the major literature gap regarding the exergy-destruction-led carbon dioxide emission responsibilities, an exergy-based model for the complete attribution of the carbon dioxide emission responsibility of temperature-peaking heat pumps has been developed using an exergy-destruction tree to show the expanded carbon footprint trace. The so-called exergy-tracing model comprises four CO_2 footprint backdrops. These are the thermal exergy inputs from the ambient and/or from a limited source such as waste heat; the exergy input for power generation to drive the heat pump; the exergy conversion unit (the heat pump); and useful applications downstream of the heat pump (demand exergies). The rational Exergy Management Model was applied, and the Second Law established a direct link between exergy destruction and the responsibility for nearly avoidable carbon dioxide emissions responsibility, ΔCO_2.

Equation 1-a shows that the ΔCO_2 term is directly proportional to the corresponding exergy destruction, through a proportionality (penalty) factor (k_i). It is a function of the temperature (See Equation 3).

$$\Delta CO_{2-i} = k_i \times E_{Xdesi} \tag{1-a}$$

The Rational Exergy Management Efficiency, Ψ_R, is the ratio between the demand exergy (D_x) and the supply exergy (E_x) and provides another direct link between ΔCO_2 and exergy destruction:

$$\Delta CO_2 = k_i \times E_X \times \left(1 - \psi_R\right) \tag{1-b}$$

$$E_{Xdesi} = Q_i \times \left(1 - \frac{T_{iapp}}{T_{i\sup ply}}\right) \tag{2}$$

$$k_i = f(T_{i\sup ply}) = 1.1 + 0.0024 \times \left(T_{i\sup ply} - T_{ref}\right)$$

$$\{T_{ref} \leq T_{isupply} \leq 700\text{ K}\}\text{ or;} \tag{3}$$

$$k_i = 1.507\varepsilon_{desi} + 0.68 \tag{4}$$

An example from the Westwood Hills Nature Center of the City of St. Louis illustrates the fundamental differences from the current literature of this model, which recognizes exergy destruction-led corresponding ΔCO_2 terms. See Table 1. In contrast, the literature on the Westwood Hills Nature Center claims that an annual operational CO_2 emission savings of more than 60% has been achieved, based on 'energy savings' (First Law only) [8]. The HVAC system for this 1260 m^2 building project (See Figure 1) includes a ground-source heat pump, radiant floor panels, and PV panels. The reported savings rate was limited to the First Law. PV panels generate electric power at a modest first-law efficiency, and the remaining solar exergy is rejected to the ambient without any useful work obtained. The missed thermal power generation opportunity must be offset by either a boiler or a solar flat-plate collector (FPC) to recover the rejected heat's exergy. Table 1 presents typical CO_2 savings as a function of the ΔCO_2 emission responsibility. Grid power has no mitigation potential. Flat-plate collectors (FPCs) and grid power are included for reference. A PV panel generates power at a modest efficiency, like 0.2. The remaining portion of the total solar exergy is destroyed and must be offset by other equipment, such as a boiler. A heat pump uses high-exergy power and generates only thermal exergy of lower value. Even if the *COP* is greater than 1, exergy destruction still occurs. Table 1 shows that the ratio of the ΔCO_2 terms revealed by the exergy-based model is substantially greater than the CO_2 emissions or savings according to the First Law. These results show the importance and essence of the new model.

Fig. 1. Net-Zero Certified Building [8]

Table 1. Actual CO_2 Mitigation Ratios of Typical Energy Conversion Equipment When the Second Law is Considering the ΔCO_2 term

Equipment	Apparent CO_2 mitigation potential (First Law)	ΔCO_2 Responsibility	$R = \Delta CO_2 / CO_2$	Correction factor for CO_2 mitigation of the original claim 1/(1+R)	Corrected mitigation potential
	kg CO_2/kW_{en}-h				
PV*	0.5	2.0	4	0.2	0.1 kg CO_2/kW_{en}h
Heat Pump	0.6	0.56	1.3	0.43	0.26
Flat-plate collectors	0.23	1.32	5.74	0.15 %	0.034
Grid Power	(-) 0.3 (no saving)	0.54	1.42	no saving	none

* Replacing grid power from a natural gas power plant and assuming that on-site PV panels feed the grid at the plant first.

When the installed capacities of PV panels and the ground-source heat pump, alongside the grid power exchange, are considered, the claimed emission savings need to be corrected by the factor (R). See Table 1. Then, the 60% savings claimed by the Author [8] are reduced to 26%. Furthermore, ground heat exchangers, PV panels, and radiant floors are embodied-CO2-intensive systems and equipment. In addition, the pumping needs for the thirty-two vertical bores in their project (76 m deep) consume a considerable amount of electrical energy. A life-cycle proration of the embodiments and emission responsibility of the borehole pumps further reduces the actual savings. Therefore, it is prudent to conclude that the actual emission savings will be less than 20%.

Kalkan et al. describe a similar project in their new system installed at the Highfield campus of the University of Southampton [9]. This system is an addition to the existing mini-CHP district energy system, with PV panels and heat pumps. This addition is identical to the configuration of the previous case. The PV+HP combination is like the data presented in Table 1. In both cases, PV panels destroy thermal exergy downstream, and heat pumps destroy most of the electrical power exergy upstream of heating or cooling. Figure 2 shows the conven-tional heat pump system in heating mode, as described by Kalkan et al. [9]. The measured COP is about 3.7.

This low COP value is responsible for DCO2 emissions, which contradicts the general statement reproduced below [10]:

'.. Studies have also shown that HPs have the potential to greatly reduce greenhouse gas emissions, particularly those of CO_2.'

These two cases refer only to the First Law of thermodynamics and ignore the ΔCO_2 component. This is a result of the misconception that renewable energy systems, such as solar energy, are free of CO_2 emissions during operation, except for their embodied emissions [11]. Despite such gaps between theory and practice, heat pumps are seeing increasing sales in EU countries. For example, the United Kingdom announced its target to install 600,000 heat pumps by 2028. Regulators claim that even when fossil-fuel-based electricity powers the heat pump, it consumes only one-third (mitigation potential of 2/3) as much as a boiler would [12, 13]. Such a claim is based solely on 1/*COP* in heating mode, yielding a savings of 0.60 after accounting for some parasitic losses. In fact, Table 1 shows a correction factor of 0.43 for the heat pump, which excludes the exergy destructions at the grid power plant: 0.60×0.43 = 0.26. When these exergy destruction-led ΔCO_2 values are also incorporated, the net mitigation potential becomes less, or even negative, depending on the central power plant mix, and depending on the fossil fuels used. If renewable energy systems provide the electricity, the condition may only slightly improve, because these systems also carry ΔCO_2 terms.

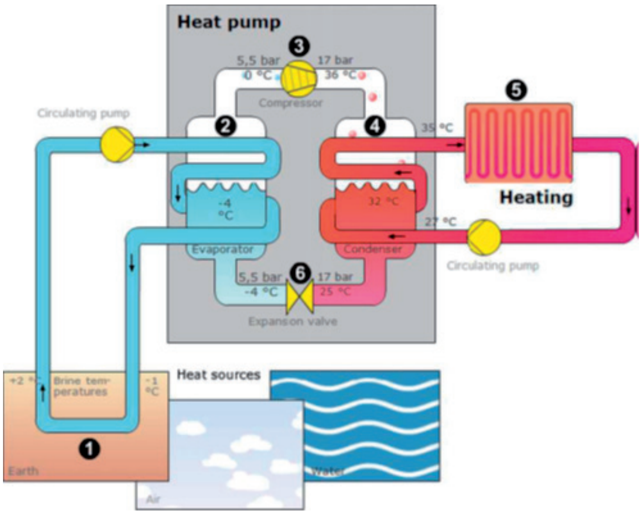

Fig. 2. Layout of a Heat Pump System in the Heating Mode [9]

Fig. 3 shows the thermal layout of a temperature-peaking heat pump that does not mitigate emissions, even though it may receive power from onsite solar PV panels and utilize waste heat. In particular, solar PV roof tiles with an unverified first-law efficiency of 0.25, connected to heat pumps, are lately claimed to achieve 20% energy savings [14]. But they ignore ΔCO_2 and emissions responsibilities. In addition, they did not account for the exergy deficit of electric-powered fans used to circulate air beneath the tiles to preheat outdoor air before it enters the heat pump. For this case, the waste heat in Figure 3 is replaced by thermal solar energy absorbed by the roof tiles, leading to a solar photo-voltaic-thermal system, PVT. The temperature-peaking *COP* of the heat pump must be at least 11 to maintain an exergy balance between the electric and thermal powers supplied [15].

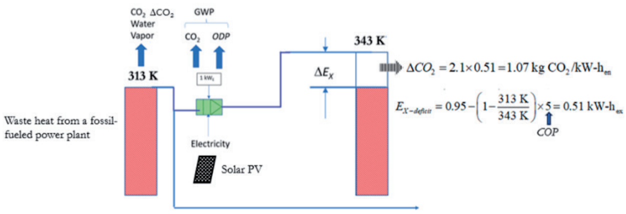

Fig. 3. Primary Exergy Destruction in a Temperature-Peaking Heat Pump

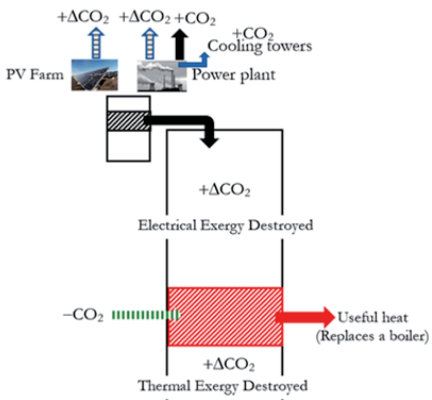

Fig. 4. The Past and The Present of CO_2 Emissions: The Responsibility of a Heat Pump

The past and current CO_2 emissions of a heat pump are shown in more detail in Figure 4. This carbon-tracing model comprises four CO_2 footprint backdrops, shown in the CO_2 emission tree in Figure 5.

1- Input Exergies for Heat, E_X: This first backdrop concerns thermal exergy utilized from ambient heat or a limited source like sewer heat at an amount of Q_1 and the source temperature *Ts*.

2- Input Exergies for Power, E_{XS}: This backdrop concerns input fuel, renewables, or waste power, including steam (electrical or mechanical), at an amount Q_2, for generating the electric power necessary to drive the heat pump. This power is used internally by the heat pump at backdrop 3.

3- Exergy Conversion, HP: Heat Pumps, power-to-heat (or cold).

4- Applications. Demand Exergies, D_X: The model associates the CO_2 trace with application selection and temperature matching, and optimizes this final backdrop downstream of the heat pump, including exergy destructions at demand points and processes.

The exergy flow bar of each backdrop is shown in Figure 5. These backdrops are holistically combined to form the most general (complete) CO_2 footprint model for heat pumps. Each diagram on the ideal Carnot cycle equivalent temperature scale shows all possible emission responsibilities, which render nearly avoidable CO_2 emissions, namely, $+\Delta CO_2$. T_{ref} is the return temperature to the ambient (sink) or the limited thermal exergy source. In this trace model, the heat pump and the input exergy (1) replace natural gas-fired condensing boilers, rendering carbon mitigation of $-CO_2$. The complete trace ΣCO_2 is $+\Delta CO_2$ $-CO_2$. There are eight major exergy destructions, including parasitic losses and grid losses. Each is responsible for ΔCO_2. T_f is the source temperature and establishes the vertical axis in Figure 5; it may be represented by a virtual source temperature, T_f^*, for non-thermal energy sources such as wind energy.

$$k_i = 1.507\varepsilon_{desi} + 0.68 \tag{5}$$

$$COP_{HP} = \left(a - b\left|T_{D1} - T_{S1}\right|\right) \tag{6}$$

$$COP_{HP_{corrected}} = COP_{HP} \times F_c = \left(a - b\left|T_{D1} - T_{S1}\right|\right) \times F_c \tag{7}$$

$$F_c = \frac{\dfrac{COP_{HP} \times \left(1 - \dfrac{T_{H2}}{T_{H1}}\right)}{0.95 + \left(COP_{HP} - 1\right) \times \left(1 - \dfrac{T_{ref}}{T_S}\right)}}{COP_{HP} \times \dfrac{\left(1 - \dfrac{T_{H2}}{T_{H1}}\right)}{0.95}} \tag{8}$$

$$E_{Xj} = \varepsilon_j \times Q_j = \left(1 - \frac{T_{1j}}{T_{2j}}\right) \times Q_j \tag{9}$$

Specific steam exergy: Sometimes, waste steam may also be used as a limited exergy source. Then Equation 10 determines the unit supply exergy from the waste steam.

$$\varepsilon_{steam} = \left(2676 + 1.60 \times \left[T_{steam} - T_{sat}\right]\right) - 7.2 \times T_{steam} \tag{10}$$

$$\varepsilon_{steam} = \frac{E_{Xsteam}\left[\text{kW-h}_{ex}/\text{kg}\right] \times \dot{m}_{steam}[\text{kg/h}]}{\dot{Q}_{steam}[\text{kW}]} \tag{11}$$

From equations 10 or 11:

$$T^{'}_{f-steam} = \frac{T_{ref}}{1 - \varepsilon_{steam}} \tag{12}$$

Virtual pressure temperature: The compressor of a heat pump may be driven by a pressurized fluid. In terms of the ideal Carnot cycle, a thermal equivalent, the virtual source temperature, T'_p, may be expressed for a unit source volume ($V = 1$) at a pressure P_f, reference environment temperature, T_{ref} (283 K), and the reference pressure, $P_{ref,}$ which is equal to one atm (1.01×10^5 Pa). T_p is using the potential and thermal energy analogy.

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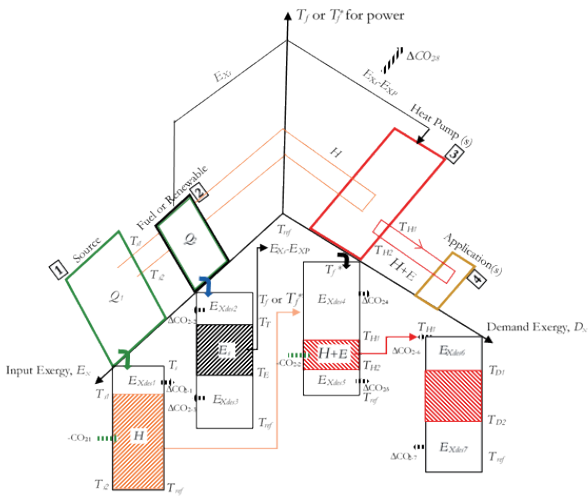

Fig. 5. Exergy-Based Complete CO2 Emission Tree of a Temperature-Peaking Heat Pump.

$$T^{'}_{p} = \frac{T_{ref}}{1 + c'\left(1 - \dfrac{P_f}{P_{ref}}\right)} \tag{13}$$

Here, c' is a combined constant involving the conversion of units, unit exergy of potential (mechanical) energy, which is 0.95 kW_{en}-h/kW_{ex}-h, and $P_{ref.}$

Sensitivity and emission analysis: The COP value of a heat pump is crucial for sizing it for design conditions and for minimizing its CO_2 and ΔCO_2 emission responsibilities. For a given thermal load, the size, and therefore the ozone-depleting potential and global warming potential due to refrigerant leakage, decreases. The available supply temperature to the heat pump, $T_{sup,}$ is important, namely, CO_2, and ΔCO_2.

$$COP = a - b \times \left(T_{\sup} - T_R\right) = a - b \times \Delta T_{peak} \tag{14}$$

$$\frac{\partial COP}{\partial T_{\sup}} = -b \tag{15}$$

$$\Delta CO_2 = k_i \times \left(\frac{0.95}{COP} - \left[1 - \frac{T_{ref}}{T_{\sup}}\right]\right) \tag{16}$$

$$\frac{\partial \Delta CO_2}{\partial COP} = -k_i \times \left(\frac{0.95}{COP^2}\right) \tag{17}$$

$$\frac{\partial \Delta CO_2}{\partial T_{\sup}} = \frac{\partial \Delta CO_2}{\partial COP} \cdot \frac{\partial COP}{\partial T_{\sup}} = \frac{0.95 \times k_i \times b}{\left[a - b\left(T_{\sup} - T_R\right)\right]^2} \tag{18}$$

In Equation 18, the term (T_{sup}-T_R) is the temperature peaking demand, D$T_{peak,}$ from a heat pump. The higher the peaking temperature is, the higher the sensitivity of the ΔCO_2 emission responsibility. On the other hand, ΔTpeak depends on T_{sup} due to COP considerations. For example, if the reservoir temperature, $T_{sup,}$ is too low, an exceedingly elevated temperature, T_{app}, required by a certain application may compromise the COP extensively (See Equation 13). The pressure loss for the pumping circuitry between the reservoir and the application service of a heat pump is given in Equation 19. Furthermore, the pumping-related power demand and, thus, the CO_2 emissions from a grid can be expressed in terms of T_{sup}. (Equations 20 and 21).

$$\Delta T_{peak} \le e T^{f}_{\sup} \tag{19}$$

$$\Delta P = c \Delta T^{d}_{app} = c\left(e \times T^{f}_{\sup}\right)^{d} \tag{20}$$

$$CO_2 = c_K \times PEF \times c \times e^{d} \times T^{f+d}_{\sup} \tag{21}$$

Fig. 6 shows Equations 17 and 21 in terms of T_{sup} for a typical set of design and operational variables.

$$\frac{\partial CO_2}{\partial T_{\sup}} = c_K \times \frac{PEF}{\eta_{Ip-m}} \times e^d \times (f+d) \times T_{\sup}^{(f+d-1)} = Z \times T_{\sup}^{(f+d-1)} \quad (22)$$

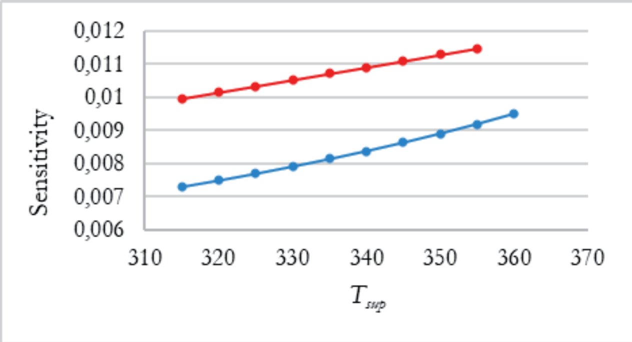

Fig. 6. Sensitivity of Emissions with T_{sup}.

Fig. 6 shows that both emission sensitivities increase with T_{sup}, thus DT_{peak}. The same relationship also holds for the CO_2 and ΔCO_2 terms. Therefore, for a given T_R, the maximum peaking temperature is limited and requires demand-side management to bring the temperature as close as possible to the resource temperature.

Sometimes the heat pump is supplied by a finite heat source. An example is seasonal thermal storage in an underground aquifer within the district energy system in Haarlem, the Netherlands [16, 17, 18]. In a similar case, Rosato et al. simulated a district solar heating and cooling system for heating, cooling, and domestic hot water in six buildings in Naples [19]. The system includes FPCs, PVs, seasonal borehole storage, and electrical energy storage. Using only the First Law, they concluded that CO_2 emissions are reduced by about 38.4%. Yet, for the renewable energy systems shown in Table 1, with their ΔCO_2 emission responsibilities, the actual CO_2 emission savings are about 20% lower than their claim. The underground seasonal aquifer system is modeled in Figure 7. The heat pump with the given *COP* properties peaks the resource temperature, T_R (in the aquifer), at T_{sup}, corresponding to the floor-heating temperature in the building.

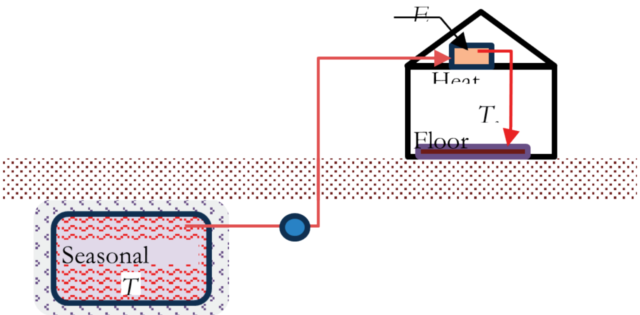

Fig. 7. A Building with Seasonal TES, Floor Heating, and a Heat Pump

T_{app} is ideally equal to T_{sup}. The aquifer is assumed to be perfectly insulated. Let X amount of thermal energy be delivered from TES. The power demand of the circulation pump is ignored. Let the original thermal energy stored be equal to Y. Let the thermal energy already used in the TES be equal to the term (Y). Regarding the actual benefits of underground thermal energy storage, concerning the exergy extracted from TES and delivered to the building(s), the question is whether the left-hand side of Equation 23 is greater, equal, or smaller than the right-hand side of the same equationThe right-hand side represents the initial condition, and when the TES is full, and the heat pump has not yet started to operate to peak supply temperature (X=0).

$$(Y-X)\times\left(1-\frac{T_{ref}}{T_R^{'}}\right)+Q_{app}\times\left(1-\frac{T_{ref}}{T_{\sup}}\right) <=>?\ Y\times\left(1-\frac{T_{ref}}{T_R}\right) \quad (23)$$

Left in the Tank Supplied to Building Full Tank

$$\Delta T_{peak} = T_{sup} - T_{R}, \quad (24)$$

$$Q_{app} = \frac{X}{\left(1-\frac{1}{COP}\right)} = \frac{X}{\left(1-\frac{1}{a-b\Delta T_{peak}}\right)} \quad (25)$$

The denominator in Equation 25 represents the thermal contribution by the electrical energy consumed by the compressor to Q_{app} in the heating mode. However, the electrical energy consumed by the heat pump has an exergy destruction penalty because the heat pump (power-to-heat system) destroys exergy upstream of the thermal exergy that it delivers. Therefore, Equation 25 is corrected such that Q_{app} is given by Equation 26. Here, 283 K is the reference temperature, T_{ref}.

$$Q_{app} = \frac{X}{\left(1-\frac{1}{COP}\right)} = \frac{X}{\left\{\left(1-\frac{1}{a-b\Delta T_{peak}}\right)\times\left(0.95-\left(1-\frac{283K}{T_R^{'}+\Delta T_{peak}}\right)\right)\right\}} \quad (26)$$

Dividing both sides by Y, and taking Y arbitrarily to be unity:

$$(1-X)\times\left(1-\frac{T_{ref}}{T_R^{'}}\right)+\left(X\left[1-\frac{1}{\left(a-b\Delta T_{peak}\right)\times\left(\frac{0.95}{COP}-(1-\frac{T_{ref}}{\left(T_R^{'}+\Delta T_{peak}\right)}\right)}\right]^{-1}\right)\times\left(1-\frac{T_{ref}}{T_R^{'}+\Delta T_{peak}}\right) <=>?\ \left(1-\frac{T_{ref}}{T_R}\right) \quad (27)$$

$$T_R^{'} \square \left(T_R - T_{ref}\right)\times\left(1-\dot{X}\right)+T_{ref} \quad (28)$$

The decision concerning Equation 27 is a function of DT_{peak}, and (X). The right-hand side of the equation is constant for given T_{ref} and T_R. According to Figure 8, for a temperature peaking, DT_{peak} of 5 K, the TES operation is limited to X=0.75. This means that if the heat pump continues to extract thermal exergy from TES, the net emission responsibility becomes positive. In other words, otherwise, if the system continues operating, it will be responsible for ΔCO_2, because the exergy on the RHS of Equation 27 will be less than that on the LHS, corresponding to the initial condition (no thermal discharge from the TES tank). This means the TES tank volume will be effectively used until the tank is discharged up to 75%. Therefore, the tank size must be proportionately larger to utilize the full thermal energy from the initial thermal charging, leaving a margin of about 25% in the tank. When DT_{peak} is set to 10 K, the X limit is slightly lower. However, for higher DT_{peak} values, such as 15 K, using TES will not be exergy-efficient.

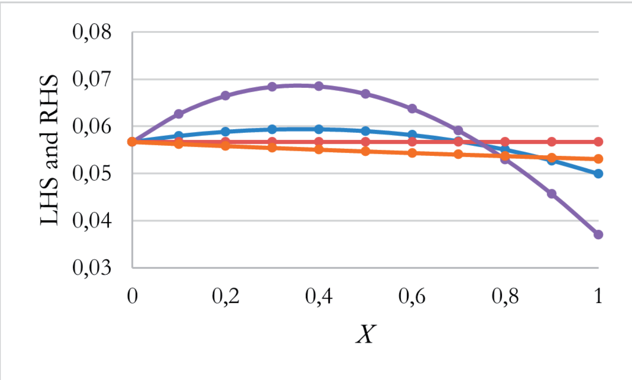

Fig. 8. Permissible X is a Function of ΔT_{peak}. T_R =300 K. T_{ref} = 283 K, a =4, b =0.02 K^{-1}

The peak exergy rationality occurs at X = 0.36 for ΔT_{peak} = 5 K. Figure 8 further shows that, for low-enthalpy thermal energy sources ΔT_{peak} must be small to utilize the maximum energy stored in TES for no ΔCO_2. Figure 9 repeats Figure 8 for T_R = 320 K and shows that the TES performance is also sensitive to the resource temperature. For example, the X value is higher (>0,9) and almost the same across the tree ΔT_{peak} cases. TES for ΔT_{peak} = 15 K also becomes exergy rational. Changes in ΔCO_2 also diminish. Therefore, any change in the TES resource temperature during charging must be closely monitored. Results may also change with the specific performance parameters of the heat pump used, namely (a) and (b). The heat pump has a cooling *COP* of four at design conditions. For 1 kW_{en}-h of cooling at 7°C/12°C (280 K/285 K) regime, the heat pump requires 0.25 kW_{en}-h of solar electricity generated by the PV panels on board, with a first-law efficiency of 0.20.

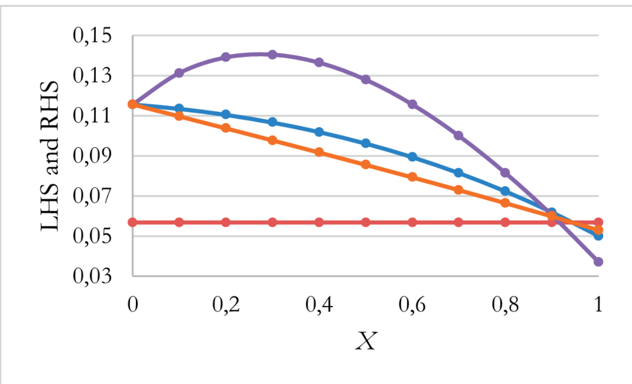

Fig. 9. Permissible X is a Function of ΔT_{peak}. T_R =300 K. T_{ref} = 283 K, a =4, b =0.02 K^{-1}

These results underline the importance of the Second Law and show that, from an exergy perspective the rate of temperature peaking must be carefully determined. If this temperature provides a T_{sup}, which is below the demand temperature, then the rest of the solution must be continued at the selection of the equipment type and size step on the demand side (in this case the building) by closing the temperature gap, either by oversizing the floor panel in terms of closer heat transfer tube spacing [20] or a different type of heating unit [21].

3. Results

The case study shows that comfort cooling using a heat pump driven by on-site (Roof type) photovoltaic panels results in CO_2 emissions per kW_{en}-h of cooling, including latent loads from dehumidification. Figure 10 shows the system's general layout. Although the system saves energy and eliminates the use of fossil fuels, exergy destructions, namely $E_{X\text{-}1}$ and $E_{X\text{-}2}$, lead to $\Delta_{CO2\text{-}1}$ and $\Delta_{CO2\text{-}1}$.

The unit exergies for cooling and electricity are 0.0106 kW_{ex}-h and 0.95 kW_{en}-h, respectively. For heat pump:

$$E_{X-PV} = 0.25\ \mathrm{kW}_{en}\text{-h} \times 0.95\mathrm{kW}_{ex}\text{-h/kW}_{en}\text{-h} = 0.2375\ \mathrm{kW}_{ex}\text{-h}$$

$$E_{X-des2} = 0.2375\ \mathrm{kW}_{ex}\text{-h-}0.0106\ \mathrm{kW}_{ex}\text{-h} = 0.2269\ \mathrm{kW}_{ex}\text{-h}$$

$$\Delta CO_{2-2} = 2.1 \times 0.2269 = 0.4765\ \mathrm{kg\ CO_2/h}$$ For PV Panel:

$$E_{X-des1} = \left(\frac{0.25}{0.2}\right) \times \left[0.95\text{-}(1\text{-}0.2) \times \left(1\text{-}\frac{283\ \mathrm{K}}{340\ \mathrm{K}}\right)\right] = 0.816\ \mathrm{kW\text{-}h_{EX}}$$

$$\Delta CO_{2-2} = 1.1 \times 0.816 = 0.8976\ \mathrm{kg\ CO_2/h},$$

$$\sum \Delta CO_{2-2} = 1.1 \times 0.816 = 1.374\ \mathrm{kg\ CO_2/h}$$

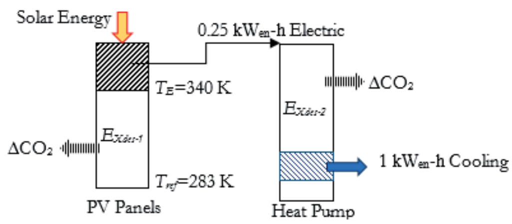

Fig. 10. Exergy Destructions in a PV-Driven Heat Pump System for Comfort Cooling. *COP*=4

On the other hand, this system replaces the on-site generator, with 0.35 efficiency, using natural gas:

$$CO_{2-saving} = \left[\frac{0.25}{0.85} \times 0.2 + 1.1 \times (0.87 - 0.95 \times 0.35)\right] = 0.5631\ \mathrm{kg\ CO_2/kW\text{-}h}$$

According to this calculation, replacing a chiller with a heat pump does not change emissions. Consequently, the net CO_2 emission responsibility will be +0.8109 kg CO_2/kW_{en}-h for comfort cooling. This is a negative CO_2 mitigation potential, although the systems seem carbon-free, without embodiments. Results show that even if renewable energy systems are completely used, unless higher *COP* values are achieved in the heat pump industry, heat pumps do not save emissions in the energy stock when the second law is considered. However, this law also offers better solutions, such as using the heat from a solar PVT panel. In this case, the low-enthalpy heat may drive an adsorption cooling machine (ADS) for sensible cooling and a desiccant wheel, both of which replace the functions of a heat pump. This alternative is shown in Figure 11. Table 1 compares the results of Figures 10 and 11. The desiccant wheel utilizes exhaust cold and little electricity. [22]. Table 2 shows that the alternative solar cooling system mitigates CO_2 emissions, with the heat pump accountable for those emissions. The overall difference between these two systems is 1.616 kg CO_2/kW_{en}-h of cooling. The parasitic power and heat of the ADS system are ignored. The ADS system's waste heat regenerates the desiccant system.

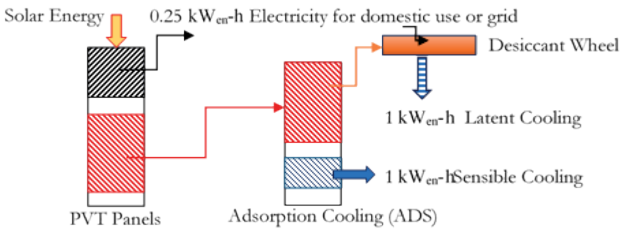

Fig. 11. Alternative Solar Cooling System Without a Heat Pump

Table 2. Comparison of Figures 10 and 11.

System	CO_2	$\sum CO_2$	Net Emissions
	kg CO_2/kW_{en}-h		
Figure 10 (Heat Pump)	-0.5631	+1.374 (PV)	+0.8109 (no mitigation)
Figure 11 (Solar PVT)	-0.5631 -(0.25/0.85×0.2)* =-0.622	~0 (PVT) -2.1×(0.25/0.2)×[0.95/4-(1-283 K/340K)] =-0.183	-0.622-0.183 =-0.805 (mitigation)

* Replaces both a generator and a boiler

4. Discussion of results and conclusions

The results of the exergy-based model, when applied to the case studies, show that the current practice of using solar energy with heat pumps results in emissions rather than a sustainable mitigation strategy. The second law of thermodynamics showed that the case study about the comfort cooling system of the nature center building with ground source heat pumps and photovoltaic panels is responsible for emissions by 0.81 kg CO_2 emissions/kW_{en}-h, rather than saving 1.616 kg CO_2/kW_{en}-h by an alternative without a heat pump, comprising solar photovoltaic panels, adsorption cooling, and desiccant wheel. The graphical display in Figure 5, namely the exergy-based complete CO_2 emission tree for a temperature-peaking heat pump, shows the number of ΔCO_2 emission points in such an application and helps designers identify and minimize them. There are four primary exergy destruction points: the source, the fuel or renewables, the heat pump, and the demand point. The corresponding exergy flow bars show that renewables are not free of $\Delta CO_{2,}$ but can be minimized. For example, a PV panel may be replaced by a PVT panel if the climate and solar insolation are suitable.

These examples show that the crucial gap in the literature on global warming is the lack of understanding of the direct link between destruction and CO_2-emission responsibility, named ΔCO_2. In the energy sector, ΔCO_2 is generally higher than direct CO_2 emissions at the source, meaning that as long as the literature gap exists, the global warming issue will not be properly resolved, because the root causes of ΔCO_2 will be kept hidden, leading to missed solution opportunities concerning minimizing exergy destructions, thus CO_2 emissions. A for CO_2. This research aims to provide in-depth insight and greater awareness of the ΔCO_2 term in the quest to achieve the Paris Agreement goals on time and sustainably. The exceedance of ΔCO_2 is exemplified in Table 1. The correction factor for the standard *COP* definition, $F_{c,}$ is also important. Equation 8 gives this value for the following sample input data:

$$F_c = \frac{\dfrac{4\times\left(1-\dfrac{310\text{ K}}{330\text{ K}}\right)}{0.95+(4-1)\times\left(1-\dfrac{283\text{ K}}{340\text{ K}}\right)}}{4\times\dfrac{\left(1-\dfrac{310\text{ K}}{330\text{ K}}\right)}{0.95}} = 0.724$$

Therefore, the corrected *COP* becomes 4 × 0.724 = 2.84.

This result reflects the actual CO_2 emissions. If the electric power comes from a natural gas power plant and the Primary Energy Facor, *PEF* for EU countries is equal to 2.5, the CO_2 emission due to power demand by a heat pump with an uncorrected *COP* of four will be 0.173 kg CO_2/kW_{en}-h, instead of 0.125 kg CO_2/kW_{en}-h, which is what the sector calculates by using the First Law. When the difference of 0.048 kg CO_2/kWh_{en} is multiplied by 600,000 heat pumps to be installed in the United Kingdom until 2028, it means that 144 tons of CO_2 per hour will remain unaccounted for. Figure 6 shows that, when operating heat pumps at varying supply temperatures, the control may not be sufficient to minimize emissions due to the high sensitivities of both CO_2 and ΔCO_2. In addition, the demand side must be dynamically managed to stabilize the supply temperature and better meet demand. For example, a heat pump-assisted heat recovery system operates under varying outdoor and indoor conditions, and the supply temperature to the heat pump varies, along with the demand temperatures on the supply side of the heat pump [23]. Therefore, the heat recovery unit must be controlled to stabilize temperatures and reduce the heat pump's sensitivity.

An important result from modeling an underground labyrinth TES coupled with a heat pump is that the available seasonal thermal energy storage is limited. It depends on the stored heat temperature and the required peaking temperature. The higher the stored heat's temperature, the lower the effect of this constraint. Results may also depend on the performance parameters of the heat pump, namely (a) and (b). Future studies will focus on the impact of these parameters on the thermal energy's usability in the TES tank.

In conclusion, this research has provided important clues for the design, selection, and control of temperature-peaking systems and equipment using heat pumps and thermal energy storage of low-enthalpy energy sources, which are abundant but remain largely untapped. The total electrification strategy and transition to green energy sources and systems see heat pumps as a key asset for decarbonization efforts. However, this paper shows that, from an exergy destruction perspective, particularly in the power-to-heat process of a heat pump, the *COP* must be higher to reduce the exergy destruction-led ΔCO_2. Thermal energy storage is seen as another important asset in utilizing waste heat sources. However, if the source is limited for a given period, such as seasonal thermal energy storage systems, the stored thermal energy may not be fully utilized during the heating season. The example of the underground thermal energy storage system in the Haarlem district receives heat from heat pumps operating in cooling mode in summer and stores it in an aquifer. Therefore, the thermal capacity is limited depending on the rejected heat from heat pumps. This makes its design and operation crucial to the system's performance and dependent on the cooling and heating degree hours of the specific climatic region. In the heating season, no further thermal energy is received. Firstly, such systems are effective if the heating and cooling degree hours are similar, and the reject heat temperature is high enough. Secondly, the useful part of the thermal energy stored depends on the peaking temperature required for the given systems and equipment used in the buildings. Sample results indicate that the peaking temperature may be responsible for ΔCO_2 emissions, which have not been accounted for in the district heating, heat pump, and thermal energy storage industries. Furthermore, the selection of the location of central TES systems, the distance between the aquifer and the district, and the piping type and size are important, because the required pumping power using electricity with a high unit exergy relative to the thermal energy stored may result in a large ΔCO_2 responsibility. The carbon mitigation potential of heat pumps and solar energy systems is lower than first-law calculations predict. A correction factor for the coefficient of performance has been developed, accounting for the exergy destruction and the potential for emission avoidance of a typical heat pump with respect to its electrical and ambient thermal inputs. This correction factor is easy to implement and is expected to resolve the ΔCO_2 emission issue in the heat pump sector, enabling more realistic predictions of decarbonization potential in the field. Further studies may focus on reviewing decarbonization directives and standards to incorporate the second law alongside the First Law. Some efforts in this respect are already documented in the literature, such as the Science Europe report, which describes the situation and urges industry to consider exergy. In the same vein, the net-zero definitions must be revised to ensure these buildings become truly net-zero in terms of exergy. In this quest, however, the ΔCO_2 terms play a significant role in the built environment and should not be neglected. In future works about heat pumps, district energy systems, thermal energy storage, and carbon footprint calculations, the Second Law must complement the current methodologies, guidelines, and standards so that the Paris Agreement goals are met on time and on a sustainable basis by taking into account the new opportunities hinted at by the Second Law. At the same time, the *COP* values need to be improved technologically, and a closer match between the supply and demand temperatures needs to be established to minimize exergy destructions. Thermal energy storage systems must also be evaluated and designed in accordance with the Second Law, and sized and operated accordingly. Furthermore, the model presented in this article analyses exergy transfer in a TES system and identifies exergy destructions beyond a certain limit of thermal exergy use in the TES system. Such an analysis is not present in the open literature because all calculations depend on the quantity of energy (First Law), and field measurements are recorded by conventional calorimeters that solely measure the quantity of heat transferred, without accounting for the temperatures, which are essential for calculating exergy transfer. Because of this shortcoming, while such data is not available, presenting any field support was not possible. Therefore, it is recommended that future studies include exergy meters.

5. Nomenclature

a, b	Linearized performance (*COP*) factors of a heat pump
c'	Coefficient in Equation 13
c_K	Carbon factor of fuel, kg CO_2/kW$_{en}$-h
CO_2	Carbon dioxide emission, kg CO_2/kW$_{en}$-h
COP	Coefficient of performance
COPEX	Exergy-based *COP*
D_X	Demand Exergy, kW$_{ex}$-h
E_X	Input exergy for heat, kW$_{ex}$-h
E_{XS}	Input exergy for power, kW$_{ex}$-h
F_C	Correction factor for *COP*
k	ΔCO_2 penalty ctor for exergy destructions, kg CO_2/(kW$_{ex}$-h/kW$_{en}$-h)
P	Pump energy, kW$_{en}$-h
P_f	Pressure, Pa
Q	Thermal energy, kW$_{en}$-h
PEF	Primary energy factor
R	$\Delta CO_2/CO_2$
R_{EX}	Exergy-based renewable energy mix in the energy sector of a given region or country
T	Temperature, K
T_a	Outdoor air temperature, K
T'_p	Thermal equivalent, virtual source tem perature of a pump, K

T_{ref}	Reference environment temperature, K
T_f	Adiabatic flame temperature of the fuel, source temperature, K
T_f^*	The Carnot-Cycle-equivalent source temperature, K
X	Amount of thermal energy received from the thermal energy storage system, kW_{en}-h

Greek Symbols

η_I	First-Law efficiency
ΔCO_2	Nearly avoidable CO_2 emission respon sibility, kg CO_2/kW_{en}-h
ε	Unit exergy, kW_{ex}-h/kW_{en}-h
ψ_R	REMM Efficiency
ΣCO_2	Total (or net) emission, $+\Delta CO_2+CO_2$, or $+\Delta CO_2-CO_2$.

Subscripts

app	Useful application
B	Boiler
dem	Demand
DE	District Energy
DS	District supply (Temperature)
DR	District return (Temperature)
des	Destroyed
E	Exit (Temperature) from useful application
en	Energy
eq	Heating equipment
ex	Exergy
H	Heat
HP	Heat pump
max	Maximum
R	Rational (Exergy utilization), resource
ref	Reference
res	Ambient resource
ret	Return
sup	Supply

Acronyms

ADS	Adsorption Cooling Machine
CHP	Combined Heat and power
DE	District Energy
DH	District Heating
DHW	Domestic Hot Water
EC	European Commission
EU	European Union
FPC	Flat Plate Collector
HE	Heat Exchanger
HP	Heat Pump
HRV	Heat Recovery Ventilation
HVAC	Heating, Ventilating, and Air-Conditioning
NG	Natural Gas
nZEXB	Nearly Zero Exergy Building
nZEB	Nearly Zero Energy Building
OECD	Organization for Economic Co-operation and Development
PV	Photo Voltaic
PVT	Photo Voltaic Heat (Solar Panel)
REMM	Rational Exergy Management Model
TES	Thermal energy Storage

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