Response to Comment on “Water harvesting from air with metal-organic frameworks powered by natural sunlight”

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In their comment, Bui et al. argue that the approach we described in our report is vastly inferior in efficiency to alternative off-the-shelf technologies. Their conclusion is invalid, as they compare efficiencies in completely different operating conditions. Here, using heat transfer and thermodynamics principles, we show how Bui et al.’s conclusions about the efficiencies of off-the-shelf technologies are fundamentally flawed and inaccurate for the operating conditions described in our study.

Bui et al.’s conclusions (1) about the efficiencies of off-the-shelf water harvesting technologies are based on idealized calculations or from a survey of product data, with little description on the working conditions available. They also do not discuss operation in low-humidity conditions related to our work (20% relative humidity (RH)) (2), where the operation of off-the-shelf technologies is infeasible; thus, such a comparison is meaningless. Furthermore, consistent with Gordon and Chiu (3), Bui et al. compare efficiencies defined on the basis of primary energy (or heat) and work (or electrical work) when they state differences of “one to two orders of magnitude.” This comparison is thermodynamically flawed, as the availabilities (exergies) of these two streams are different and cannot be compared directly (4). In addition, they draw conclusions solely based on our proof-of-concept demonstration while ignoring the objective of the demonstration, possible improvements, and optimizations extensively discussed in our study (2). Furthermore, although Bui et al.’s prior theoretical work on idealized multistage vacuum pump–based membrane dehumidifiers is interesting, neither their concept nor their claim of efficiency (or specific energy consumption (SEC)) has been realized experimentally (5). Here, we provide detailed responses to their comment, as well as summarize and highlight the discussions presented in our work that can lead to further improvements in efficiency.

The comparison of SECs in (1) has two fundamental errors that lead to misguided conclusions. First, Bui et al. compare the SEC defined on the basis of primary energy (or heat) for (2) to that defined on the basis of work (or electrical work) for refrigeration-based atmospheric water generators (RAWGs). The appropriate way to compare these SECs is to factor in the conversion loss from the primary energy to work (4). Although Bui et al. acknowledge the associated penalty for solar-driven systems, they do not account for it in the SEC comparison. Assuming the same photovoltaic efficiency (20%) quoted in (1), the SEC values based on primary energy input for RAWGs are 1000 to 2000 kWh m⁻³ and not 200 to 400 kWh m⁻³, which is used for efficiency comparison in (1). Second, this comparison is still inappropriate because SECs of the referenced RAWGs in (1) are evaluated at operating conditions completely different from the operating regime (20% RH) we described in (2). For instance, the specific RAWG (6) referenced in (1) operates with an SEC of 330 kWh m⁻³ (based on electrical work) at ambient conditions of 26.7°C and 60% RH, with no information available for operation in low-humidity conditions.

Bui et al. claim that efficiencies for off-the-shelf RAWGs cannot be changed by orders of magnitude as a function of the operating conditions. To illustrate this, we present results from a first-order performance estimation of a RAWG (Fig. 1). The efficiencies are represented as thermal efficiency (product of harvested water and latent heat per unit input primary energy) because this removes ambiguity between the use of primary energy and work. In our analysis, we assumed a compact fin-tube cross-flow heat exchanger with 100% fin efficiency operating with a cooling coefficient of performance (COP) of 5 (quoted in (1)) and a refrigeration temperature of 2°C. Using a wet coil–dry coil methodology (7), we determined the thermal efficiency as a function of ambient RH and temperature (Fig. 1A). At 25°C and 60% RH, the predicted thermal efficiency is ~30%. The results are comparable to product data from a representative off-the-shelf technology (6) referenced in (1): SEC of 330 kWh m⁻³ (thermal efficiency of ~38%) at ambient conditions of 26.7°C, 60% RH, and dew point of 18.3°C. Therefore, our first-order estimate enables us to understand the performance limits of RAWGs. Figure 1A shows that the thermal efficiency (or SEC) of RAWGs can indeed change by orders of magnitude under various operating conditions. These results also show that there exists a regime at low ambient RHs or temperatures where practical operation of RAWGs is infeasible. These results clearly contradict the claims in (1).

Our statements are not intended to criticize RAWGs in general. As shown in Fig. 1, they serve as viable options to harvest a sufficient amount of water in relatively high RH conditions (8). Our statements are targeted toward the unsupported claims in (1) stating that the operational efficiency for RAWGs is vastly superior regardless of ambient conditions. In fact, commercial RAWGs are not rated to operate at RHs less than ~40% or in cold weather (which lowers the ambient dew point and humidity content). Other advanced cycles are also available, such as reheated chilled air to precool processing air (6); however, this cannot drastically influence operation under these conditions. Note also that comprehensive analyses by other researchers (8, 9) have shown that the operation and efficiencies of RAWGs are tightly coupled to ambient RH and temperature, similar to Fig. 1. Their analyses suggest that practical operation for a chosen configuration of a RAWG is not possible under conditions with a dew point of ~7°C and refrigeration temperature of 1°C. This is attributable to the minimum possible refrigeration temperature as well as the performance of auxiliary components (e.g., heat exchangers) for a given system. The efficiencies of RAWGs are not solely dependent on the ambient dew point; however, it provides an estimate of the regime where practical operation is infeasible. Thus, the ambient dew point is an important factor that additionally limits operation of RAWGs in arid regions (10). For instance, under the conditions in (2)–25°C and 20% RH—the practical operation of RAWGs is infeasible because the dew point is ~0°C, and freezing water out of air is impractical.

This need to restrict operation of RAWGs to reasonably high dew points also limits the amount of water that can be extracted (recovery ratio) from the inlet air stream. This fundamental consideration is completely ignored by Bui et al., who claim that a recovery ratio (fraction of water that is

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harvested from inlet air stream) of 0.5 is realistic for a RAWG operating at ambient conditions of 35°C and 20% RH. However, this recovery ratio is far from realistic, as it leads to dew points below 0°C (evident from Fig. 1B) and hence infeasible operation of RAWGs. Furthermore, their simple calculation of SEC ([3656 kWh m\(^{-3}\)/COP, which considers the sensible and latent heat requirement] for this condition and their chosen unrealistic recovery ratio ignores the conversion loss from primary energy to work for the cooling cycle. Factoring in 20% primary energy to work conversion efficiency, their corrected SEC is (18,280 kWh m\(^{-3}\)/COP. For instance, with a more realistic recovery ratio of 0.05 to 0.1 based on a chilled air temperature of 7°C to 8°C from ambient conditions of 35°C and 20% RH, the corrected SEC range from this calculation is (60,000 to 120,000 kWh m\(^{-3}\))/COP, one to two orders of magnitude higher than the initial calculation in (1).

Sorption-based approaches can work in various operating regimes where RAWGs are infeasible. For example, at an ambient temperature of 5°C, the dew point is below 0°C until ~70% RH; however, adsorbents can still capture water from air in these conditions. Even under exceptionally dry climates where the dew point is below 0°C and RH is well below 20% during the day, the diurnal temperature swing (day-night) can provide sufficient RH for adsorbents in the night. This example indicates a superior advantage of a sorption-based approach over off-the-shelf RAWGs, which are restricted by their minimum possible chilled air temperatures (e.g., ~7°C dew point at 40% RH and 20°C ambient temperature (9)) and by the performance of their auxiliary components. Furthermore, at these conditions, the efficiencies of off-the-shelf RAWGs will be substantially worse if operational, perhaps lower than the metrics claimed in (1) by orders of magnitude.

The thermal efficiencies of our proposed approach are predicted to be around 6 to 10% at a desorption heat flux of 1 kW m\(^{-2}\) and convective heat transfer coefficients of 10 W m\(^{-2}\) K\(^{-1}\) at 20% ambient RH (from figure 3 of (2)). As discussed above, the operation of RAWGs in these conditions is infeasible. This low efficiency, however, is attributed in part to the use of a nonconcentrated solar flux (i.e., 1 kW m\(^{-2}\)) for water harvesting for simplicity (2). In addition, the thermoelectric element was used in our proof-of-concept to enable visualization through a view port, and active cooling is not necessary in a practical device operating with a sufficient desorption heat flux. On the basis of the analysis and discussion in (2), the efficiency of the adsorption-based water harvesting system can be substantially improved with (i) the choice of an adsorbent with a stepwise isotherm; (ii) a higher desorption heat flux; (iii) optimized diffusional properties (e.g., particle size, density, and vapor transport (17)); and (iv) appropriate thermal insulation to mitigate heat loss.

As evident from the MOF-801 isotherm (stepwise), the majority of water can be desorbed at a near-constant temperature. This enables the use of a greater fraction of the desorption energy for regeneration rather than heat losses. Moreover, the efficiency can be improved with higher desorption heat fluxes. For instance, with a desorption heat flux of 1.5 kW m\(^{-2}\) instead of 1 kW m\(^{-2}\), we predict a thermal efficiency gain by roughly a factor of 2 with MOF-801 under identical boundary conditions (figure 3 of (2)), as expected. This can be realized with various approaches—for solar, with stationary reflectors (22) or with thermal concentration (23) because the required concentration ratio is low. In addition, the diffusional transport can be enhanced with optimized particle diameter and density of MOF materials or with buoyancy-driven vapor transport during desorption/condensation with geometric orientation (density gradient–assisted transport rather than diffusion in stagnant air). Although the MOF-801 that we used has a crystal diameter of ~0.6 μm (2), which limits intercrystalline diffusion, MOFs with varying particle sizes can be readily synthesized. Appropriate thermal insulation, such as optically transparent and thermally insulating aerogels (14, 15) and highly absorptive coatings (e.g., Pyromark coating) for solar thermal systems, can further reduce the losses and increase the thermal efficiency.

Bui et al. indicate that sorption-based AWGs, including our study, require active cooling during adsorption. However, their statement is simply based on the enthalpy of adsorption without consideration of sorption kinetics in air. As shown in the analysis in (2), because of the naturally slow diffusion and adsorption of vapor in air, with a natural convective heat transfer coefficient of 10 W m\(^{-2}\) K\(^{-1}\), we predicted that the MOF layer temperature can be sufficiently cooled during adsorption. This is explicitly evident from figure 3 of (2); thus, Bui et al.’s statement is invalid.

Next, we address the statement in (2) that our approach has large heat losses. The net heat loss depends on the MOF layer and ambient temperatures. Under the equilibrium considerations of a temperature difference between the MOF layer and condenser for water harvesting, MOF-841, UIO-66, and PIZOF-2 (figure 1 of (2)) require ~30 K, ~21 K, and ~7 K temperature differentials, respectively. In contrast, MOF-801 requires a ~45 K differential at an ambient temperature of 25°C. Consequently, MOF-801 exhibits relatively high heat losses as a result of the higher operational temperature, whereas other MOFs operate with much lower heat losses, indicating that our assumption of negligible heat loss is reasonable (2). As a result of the stepwise isotherm of MOFs, the heat loss fraction can be further reduced with a higher desorption heat flux as discussed above. With the identical configuration used in our proof-of-concept demonstration (figure 4 of (2)), increasing the desorption heat flux from ~0.6 kW m\(^{-2}\) (solar flux × optical losses) will increase the thermal efficiency. All of the aforementioned improvements are discussed or can be inferred from our study (2).
Bui et al. also discuss other desiccant-based approaches (16, 17). However, the conventional adsorbents (e.g., zeolites and silica gels) often require high regeneration temperatures for water release or limited sorption capacity within a narrow range of adsorption/desorption conditions; as a result, the sorption characteristics of the MOFs outlined in (2) make them highly attractive. Furthermore, Bui et al. state the SEC of a desiccant-based approach (2430 kWh m$^{-3}$) without specifying the conditions at which the SEC was evaluated. The choice of MOF-801 is criticized for not being optimal because of its low adsorption capacity in comparison to other alternatives. However, as stated in (2), our choice of MOF-801 was based on its well-characterized properties and hydrothermal stability for water adsorption.

On the basis of heat transfer and thermodynamics principles, it is possible to identify several inconsistencies and inaccuracies in (1) that lead to misguided conclusions about the potential applications of adsorption-based water harvesting. The adsorption-based atmospheric water harvesting is a highly promising alternative to off-the-shelf RAWGs in dry and water-scarce regions. This is further evident when the energy input is constrained to low-grade heat [~100°C (18, 19)] and not electricity. With low-grade heat, the efficiency of both heat-to-work cycles and heat-to-cooling (e.g., adsorption or absorption chiller) cycles, which ultimately drive RAWGs, is inherently low for these sources. Atmospheric water harvesting in general is especially relevant in remote and landlocked areas. We disagree that atmospheric water harvesting in such regions would be “low-impact” (1), as it can address local water scarcity. As discussed in (2), we envision the practical operation of an adsorption-based water harvester driven by low-grade heat, operating in conditions where the use of RAWGs is infeasible. With the improvements discussed above, thermal efficiencies of ~20% are achievable in arid climates with RH < 40%.

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