TECHNICAL COMMENT

RENEWABLE RESOURCES

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

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Kim *et al*. (Reports, 28 April 2017, p. 430) presented results for the solar-driven harvesting of water from air via metal-organic frameworks as a prodigious potential advance toward remedying global water shortages. Basic thermodynamics and a survey of multiple off-the-shelf technologies show that their approach is vastly inferior in efficiency (and thereby in feasibility) to available alternatives.

Kim *et al*. (*1*) described their solar-driven harvesting of water from air as a major energy-efficient advance toward mitigating global water shortages. However, as shown here, off-the-shelf systems are more efficient. Constraining the energy input to solar does not diminish the challenges raised here because (i) commercially available solar-driven water-harvesting systems are much more efficient, (ii) any low-temperature heat source suffices, and (iii) solar collection components are costly.

Energy efficiency is commonly expressed as specific energy consumption (SEC), an overriding factor in assessing feasibility. In (*1*), the water harvester is a desiccant absorber-desorber with a particular metal-organic framework (MOF). SEC can be estimated to be >10,000 kWh m^{-3}, excluding the power for the thermoelectric cooler. It is one to two orders of magnitude higher than today's off-the-shelf alternatives.

The fundamental thermodynamic limit for dehumidification depends on (i) relative humidity (RH), (ii) ambient temperature (T_{amb}), and (iii) recovery ratio [RR = the fraction of the water vapor in the incident air stream harvested as liquid water (*2*)]. For consistency with (*1*), we consider RH = 20% and T_{amb} = 35°C (and a realistic RR = 0.5), for which SEC_{min} = 86.24 kWh m^{-3}. The leading technologies are (i) direct cooling, usually but not exclusively via vapor-compression chillers (VCCs) (*3–6*), and (ii) desiccants (*1*, *7*, *8*).

The efficiency via direct cooling is mainly limited by the energy input that unnecessarily cools the air (*3*), which worsens as RH decreases. The lower bound on SEC depends on RR, as well as on RH and T_{amb} via their influence on the coefficient of performance (COP) of the cooling system (COP = total cooling load/input power) (*2*). For the conditions from (*1*), SEC = (3656 kWh m^{-3})/COP at RR = 0.5 (*2*). Commercial VCCs achieve COP values up to ~5.5 (*9*), and the reversible Carnot limit is noticeably higher. Commercial direct-cooling systems are commonplace, with typical measured SEC values of 200 to 400 kWh m^{-3} (*4–7*). Although RH and T_{amb} for these measurements differ from those in (*1*), this difference accounts for only a small part of the disparity of more than an order of magnitude in SEC relative to (*1*). If direct-cooling systems are constrained to be solar-driven, then, with mass-produced photovoltaic system efficiencies of ~20%, the associated penalty in SEC would be a factor of ~5.

Desiccant systems must work in cycles of two heat-rejection steps and condensation, plus one heating step for regenerating the desiccant. Although sorption and condensation do not require sub-ambient cooling temperatures, high efficiency mandates externally driven active cooling, translating into non-negligible energy input for the cooling steps. Although the sorption heat is desiccant-dependent, its minimum value is water's latent heat of vaporization, ΔH_v = 694 kWh m^{-3}, independent of RR. The desiccant regeneration heat is non-negligibly higher than the water sorption heat. Restricting the energy input to solar heating would increase SEC_{min} by a factor of ~2 because mass-produced stationary solar thermal systems have a solar-to-heat efficiency of ~50% for the temperature range of interest. A representative desiccant system with simple stationary solar thermal collectors, without efficient cooling mechanisms, yielded SEC ≈ 7000 kWh m^{-3} (*8*), twice the value that we estimate from (*8*), to account for actual collection area including side reflectors. A strategy that improves upon the SEC of desiccants by combining them with active solar-powered cooling (electricity from photovoltaics and heat from solar thermal collectors) had a measured SEC of 2430 kWh m^{-3} (*10*). Water harvesting from air notwithstanding, potable water is most widely produced via reverse-osmosis desalination, with SEC values in large-scale commercial plants as low as 2.5 kWh m^{-3} (*11*). This high efficiency stems from desalination inherently being a mass-transfer/separation process rather than a thermal process (*11*). Nonetheless, reverse osmosis is not a panacea, with limited usefulness in small-scale low-impact applications (such as in areas far from the sea) and membranes that require periodic replacement.

The system reported in (*1*) is for proof-of-concept purposes only, with future prospects of improving thermal conductivity and optimizing the separation of the condenser. Even so, it is not unproblematic. First, it lacks an efficient cooling mechanism for heat rejection, which prolongs the absorption step and lowers the water production rate. Second, the sizable spacing between the desiccant and the condenser, together with inefficient cooling to drive water vapor diffusion, results in slow mass transfer. This limitation leads to a prolonged condensation step, which in turn lowers the water production rate and augments heat loss. From the data in (*1*), heat loss is ~93% of the solar input (~10,000 kWh m^{-3}), assuming that the useful required energy is ΔH_v = 694 kWh m^{-3} and that the remainder primarily represents heat loss. When Kim *et al.* assume heat loss to be negligible, they err by a factor of ~14 [1/(1 – 0.93)]. Additionally, the energy for the inherently inefficient thermoelectric cooling was not accounted for. Finally, the highlighted MOF has a low absorption capacity relative to zeolite alternatives, even for RH ≤ 20% (*8*, *10*, *12*, *13*), and their desiccant approach is not new; examples of prior studies include (*14–16*).

Part of the motivation in (*1*) is the appeal of MOFs in that their structure, and hence their adsorption properties, can be finely tuned. Moreover, the system is simple, with potential applicability in isolated arid regions. Given the exceedingly low efficiency, compounded by the far superior performance of off-the-shelf technologies, the contention of Kim *et al.* that their air water harvester is efficient or novel, solar-driven or otherwise, with the potential to affect global water shortages can be questioned.

Because of the substantial disproportion between the fundamental thermodynamic limit for the SEC of atmospheric water harvesting and the SEC values for the best processes developed to date, it is natural to ask whether other strategies could bridge the gap. We note that one such recently proposed concept is multistage vacuum-based membrane dehumidification (*2*), where a highly water-permeable and selective membrane is sandwiched between a feed channel (humid air at atmospheric pressure) and a permeate channel, with the driving force for water vapor permeation being provided by a vacuum pump, and the water being harvested in an air-cooled condenser at the saturation pressure. Basic thermodynamics and engineering show that this strategy indeed has the potential to approach the thermodynamic limit (*2*).

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