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OPINION

Reply to the 'Comment on "$ per W metrics for thermoelectric power generation: beyond *ZT*"' by G. Nunes, Jr., *Energy Environ. Sci.*, 2014, 7, DOI: 10.1039/C3EE43700K

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The Comment by Nunes suggests a welcome refinement to an approximation made in the original paper. We show here that Nunes' refinement is identical to a modified effective thermal conductivity, $k_{eff} = k(1+\gamma \cdot ZT)$, where k is the thermal conductivity, ZT is the usual material figure of merit, and γ is in the range 0.4 - 0.5. This form of k_{eff} was already identified in Section 3.3 of our original paper as an option to improve the accuracy of the calculations and is itself an approximation to the more sophisticated k_{eff} analysis of Baranowski, Snyder, and Toberer [J. Appl. Phys. 113, 204904 (2013)]. As noted by Nunes and ourselves, the main downside of such refinements is that they complicate the universality of the main result, the universal cost surface in Fig. 2 of the original paper. The simplified results in the original manuscript are justified and reasonable for $ZT \sim 1$ or less, for physical insight, scaling, and rapid screening. For the best accuracy in real systems, exact numerical solutions of the coupled cost and power equations are most appropriate, examples of which we have recently published for 30 bulk and thin film materials in *Renewable and Sustainable Energy Reviews*, **32**, 313-327, 2014.

We welcome Nunes' comments and the suggested refinement. It is important to clarify that the original paper[1] does account for the Peltier heat flows everywhere except in the approximation of the junction temperatures. The corresponding results are exact in the limit of small *ZT*, consistent with the justifications originally given. The errors introduced by this small-*ZT* simplification were discussed there in Section 3.3 by comparison with exact numerical solutions,[2] as well as with an effective thermal conductivity approach that we now show to be formally equivalent to Nunes' refinement.

To see this equivalence, rewrite Eq. (8) of the Comment using $K_{T,eff} = K_T(\zeta/2)$, corresponding to $k_{eff} = k\zeta/2 = k(1+0.5ZT)$. Here we work in terms of the familiar material *ZT*, rather than $Z_{pn}T_m = 4ZT$ as in the Comment.

The introduction of a k_{eff} to simplify thermoelectric analysis was recently considered carefully by Baranowski, Snyder, and Toberer (BST),[3] cited as Ref. [17] in the original paper. We found[1] empirically that BST's Eq. (38) is well-approximated by the convenient linearization

$$k_{eff} = k(1+\gamma \cdot ZT), \qquad (1)$$

where the constant γ is typically in the range 0.4 - 0.5. Nunes' refinement is equivalent to γ=0.5, while Section 3.3 of the original paper[1] used γ=0.395. (The best choice of γ depends weakly on the ZT and (T_1/T_2) of interest. 0.395 is optimal for $0 < T_1/T_2 \le 3$ and $0 < ZT \le 3$, ensuring errors no more than 9.2% compared to BST. However, such additional distinctions about the best γ are likely unimportant in real systems, considering the other approximations already incorporated in such lumped, constant property analyses.)

The errors introduced by the approximation of Eq. (13) of the original paper[1] were discussed in Section 3.3 for a Bi_2Te_3 case study. It is also noteworthy that the errors in locating the characteristic (L_{opt}, F_{opt}) point that marks the head of the low-cost valley are more than twice as small as the errors in the \$/W value itself. In all cases the errors vanish as $ZT \to 0$ and scale no stronger than linearly with *ZT*, confirming the basic justification of the approximation. This gradual degradation in accuracy is also evident from Eqs. (10)-(13) of the Comment. Thus, refinements in k_{eff} are most important for higher *ZT* materials, although we note that the large majority of present materials (mature enough for scalable manufacturing[2]) may still be considered to lie acceptably within a low *ZT* approximation, depending on the desired accuracy.

Both Nunes' and our derivations incorporate additional simplifications. Notable examples are (i) electrical load matching: $m \approx 1$, (ii) matched heat exchangers: $K_H \approx K_C$ ($= K_X$ in Nunes' notation), and (iii) matched n and p materials: $Z_{pn} = S_{pn}^2/(R(m+1)K_T) \approx 4S^2\sigma/k = 4Z$. Regarding the first point, the optimal m is actually slightly greater than 1 because of the Peltier and Joule heating effects on the junction temperatures as argued by Refs. 8, 14, and 15 of the original manuscript. Second, in practice it may be difficult and sometimes not even desirable to thermally-match heat exchangers. This is likely since the temperatures and fluid convective conditions may differ substantially at the heat source and sink, resulting in significantly different cost-performance scaling C_{HX} at hot and cold sides. Third, the mathematical simplicity of assuming matched materials with constant properties (k, S, and σ independent of T) outweighs the corresponding accuracy concerns for these analytical models; the Comment's shorthand Z_{pn} is simply equal to $4Z$ due to assumptions (i)-(iii).

In closing, the refinement suggested in the Comment is identical in form to the k_{eff} correction motivated by BST[3] and already mentioned in Section 3.3 of the original paper.[1] Such refinements are welcome and for typical ZT~1 improve the accuracy by typically ~10 - 20% in L_{opt} and F_{opt}, and up to a factor of ~2 in G. However, as noted in both the original paper and the Comment, the small-ZT approximation must be used to generate the universal cost design surface (Fig. 2 of the original paper) which has the benefit of being independent of ZT.

If L_{opt}, F_{opt}, and \$/W results are desired with the utmost in accuracy, the exact coupled, non-linear cost and power equations should be solved numerically, as done for a Bi_2Te_3 example in the original manuscript. Indeed, it is for precisely this reason that we recently published *exact numerical* \$/W results for 30 realistic bulk and thin film materials.[2] That study showed that the ranges of L_{opt}, F_{opt}, and optimal \$/W often span factors of 100 or more among the different materials considered, a range much larger than the analytical refinements discussed here.

Notes and references

[1] S. K. Yee, S. LeBlanc, K. E. Goodson, and C. Dames, Energy & Environmental Science **6,** 2561 (2013).

[2] S. LeBlanc, S. K. Yee, M. L. Scullin, C. Dames, and K. E. Goodson, Renewable and Sustainable Energy Reviews **32,** 313 (2014).

[3] L. L. Baranowski, G. Jeffrey Snyder, and E. S. Toberer, Journal of Applied Physics **113** (2013).

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