Catalytic Advantage in Otto-like Two-Stroke Quantum Engines

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We demonstrate how to incorporate a catalyst to enhance the performance of a heat engine. Specifically, we analyze efficiency in one of the simplest engine models, which operates in only two strokes and comprises of a pair of two-level systems, potentially assisted by a d-dimensional catalyst. When no catalysis is present, the efficiency of the machine is given by the Otto efficiency. Introducing the catalyst allows for constructing a protocol which overcomes this bound, while new efficiency can be expressed in a simple form as a generalization of Otto's formula: $1 - (1/d)(\omega_c/\omega_h)$. The catalyst also provides a bigger operational range of parameters in which the machine works as an engine. Although an increase in engine efficiency is mostly accompanied by a decrease in work production (approaching zero as the system approaches Carnot efficiency), it can lead to a more favorable trade-off between work and efficiency. The provided example introduces new possibilities for enhancing performance of thermal machines through finite-dimensional ancillary systems.

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With inspiration coming from the field of chemistry, a catalyst has been introduced in quantum information theory as an auxiliary system that expands the range of possible state transformations while remaining unchanged throughout the protocol [1,2]. Catalysis was subsequently also applied to quantum thermodynamics [3–14]. In particular, catalysis was used to enhance performance of cooling [15–17]. In the context of thermal machines working in a cyclic fashion, it emerges as the most apparent generalized thermodynamic resource.

In this Letter, we want to characterize the catalyst's ability to enhance the performance of quantum heat engines. We show that the presence of a catalyst not only boosts the efficiency, but also can drive a machine that was not working as an engine to the engine regime. Moreover, the catalyst can also increase an engine's power (i.e., work per cycle) or lead to a more favorable power versus efficiency trade-off. These results are obtained within a class of two-stroke engines closely related to the Otto engine.

The conventional Otto cycle is one of the most well-known paradigms for constructing heat engines at the microscopic scale and has been thoroughly investigated both theoretically [19–37] and experimentally [31,38–43]. Its simple operational mode is based on interaction with the environment alternating with energy-level transformations, collectively forming the four-stroke thermodynamic cycle. The central question in the Otto engine studies is how to enhance its performance. Most of the research primarily focuses on dynamical optimization, aiming to achieve a better balance between power and efficiency by considering different system-environment couplings [41,44–46]. Yet, there has been limited attention given to fundamentally improving efficiency alone, solely through a less dissipative heat-to-work conversion. In this case, there seems to be no novel ideas explored beyond the obvious approaches like the usage of the nonthermal baths [47–51].

We consider an operational simplification of the Otto cycle, which reduces it from four to just two strokes [52–59]. The fundamental concept of the two-stroke engine involves breaking down the cycle into two distinct stages: (i) work extraction through an isoentropic process and (ii) heat exchange via thermalization with heat baths. This division significantly streamlines the engine's operation, as after the work stroke the cycle can be promptly completed by bringing the working body into contact with the respective environments. The primary trade-off for this simplification is an increase in the engine's dimension. Specifically, the simplified, two-stroke engine requires simultaneous operation on the pair of two-level systems (TLSs), while only a single TLS is required for the four-stroke Otto engine. Here, we focus on the two stroke-model representing an analog of the Otto cycle. However, the concept of two-stroke engines extends beyond this, and detailed analysis, including optimality proofs, will be presented for this general model in Ref. [60].

Within this paradigm, we provide a systematic methodology for how to include a d-dimensional catalyst into an operation of the two-stroke engine that leads to the generalized "d-Otto" efficiency, given by the formula

$$\eta_d = 1 - \frac{1}{d}\frac{\omega_c}{\omega_h}, \tag{1}$$

with a positive work production for

$$d \in \left(\frac{\omega_c}{\omega_h}, \frac{\beta_c \omega_c}{\beta_h \omega_h}\right). \tag{2}$$

We identify regions of parameters (temperatures β_c and β_h and frequencies ω_c and ω_h) where the presence of the catalyst is a necessary condition for the machine to work as an engine as well as the regions where the catalyst brings higher efficiency or work production.

Although we concentrate here on engines, the idea can be easily generalized and applied for refrigerators and heat pumps as well. Generally, it opens a new range of possibilities for increasing the performance of thermal machines. Notably, in contrast to most of the other studies, in our case, the catalyst is included explicitly as the finite-dimensional system.

Two-stroke engine.—We commence by introducing a two-stroke engine, which is conceptually depicted in Fig. 1. The engine operates in two fundamental steps: the work stroke and the heat stroke. In the initial stage, two thermal systems denoted as τ_h and τ_c (coming from hot and cold bath and marked in Fig. 1 by red and blue colors, respectively) are brought into contact with a third system ρ_s (marked in green), functioning as a catalyst. The work stroke is defined as the ergotropy extraction process [61–65], where work is carried out by an external agent. Finally, during the heat stroke, hot and cold systems are thermally equilibrated, which also uncorrelates the catalyst and restores the engine to its initial state.

A mathematical description of the proposed engine is based on the following assumptions: (i) The initial state of the engine is defined as the product state: $\varrho = \tau_h \otimes \tau_c \otimes \rho_s$, where $\tau_{h,c} \propto \exp(-\beta_{h,c} H_{h,c})$ are thermal states with corresponding (inverse) temperatures $\beta_h < \beta_c$ and Hamiltonians $H_{h,c}$; (ii) a single cycle of the engine is described by a unitary process U, such that $\varrho \to U\varrho U^\dagger$; (iii) the final marginal state of the catalyst is equal to the initial one: $\mathrm{Tr}_{hc}[U\varrho U^\dagger] = \rho_s$. Then, thermodynamics of the engine is introduced based on the following exchanged heat definitions:

$$Q_{h,c} = \mathrm{Tr}[H_{h,c}(\varrho - U\varrho U^\dagger)], \tag{3}$$

which is precisely the amount of energy that needs to be provided by external baths in order to thermalize the systems. In accordance with the first law, the work that

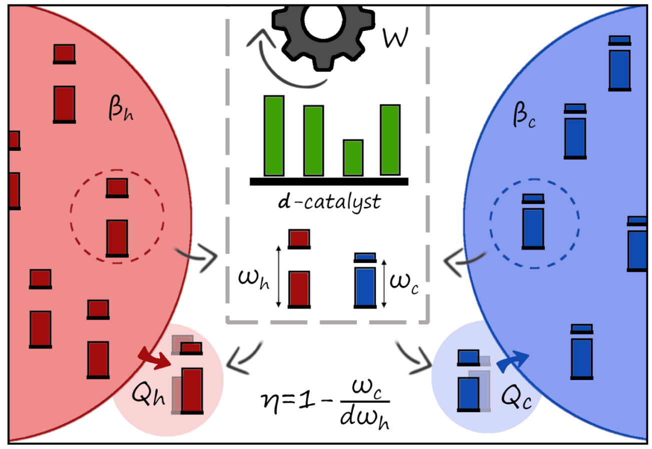

FIG. 1. Two-stroke engine assisted by a catalyst. The operational principle of a two-stroke engine is to combine thermal resources, such as hot and cold thermal two-level systems, and use an assisted catalyst to reduce the total energy of the system by performing work W on an external agent. The first work stroke is performed on an isolated system and is considered a unitary process. After that, the used fuels are removed and thermalized again, triggering corresponding hot Q_h and cold Q_c heat flows. The catalyst, after removing the fuel, returns to its initial state, allowing the entire process to be repeated. As a main result, we demonstrate that a d-dimensional catalyst can enhance the efficiency of the process to the generalized Otto's formula: $\eta = 1 - (1/d)(\omega_c/\omega_h)$.

is provided by external agent is equal to $W = Q_c + Q_h$, such that efficiency of the engine is given by

$$\eta = \frac{W}{Q_h} = 1 + \frac{Q_c}{Q_h}. \tag{4}$$

One may prove that in this framework the second law is satisfied, such that the Clausius inequality holds: $\beta_h Q_h + \beta_c Q_c \leq 0$.

In this Letter, we are interested in one of the simplest engines that consists of the hot τ_h and cold τ_c TLSs and the d-dimensional catalyst ρ_s. The initial thermal states of TLSs are $\tau_k = \mathcal{Z}_k^{-1}(|0\rangle\langle 0|_k + e^{-\beta_k\omega_k}|1\rangle\langle 1|_k)$ with Hamiltonians $H_k = \omega_k |1\rangle\langle 1|_k$, where $\mathcal{Z}_k = 1 + e^{-\beta_k\omega_k}$ (for $k = h, c$). The catalyst is described by the density matrix $\rho_s = \sum_i p_i |i\rangle\langle i|_s$ with an arbitrary Hamiltonian from d-dimensional Hilbert space. Moreover, we concentrate solely on unitary operations U given by the set of transpositions of the energy levels (the so-called swaps). For example, the swap $|ijk\rangle \leftrightarrow |i'j'k'\rangle$ corresponds to the unitary action $U|ijk\rangle = |i'j'k'\rangle$ and $U|i'j'k'\rangle = |ijk\rangle$.

Otto efficiency (without a catalyst).—Let us start with a protocol with two TLSs (without the assisted catalyst), which leads to the Otto efficiency. In this case, to extract positive work $W > 0$ via the transposition of the energy levels, there must be an inversion of the population in the composite state of $\tau_h \otimes \tau_c$. In the following, we represent the initial (diagonal) density matrix by the vector of probabilities $\vec{p}_0 = (\mathcal{Z}_h \mathcal{Z}_c)^{-1}(1, e^{-\beta_h \omega_h}, e^{-\beta_c \omega_c}, e^{-\beta_h \omega_h - \beta_c \omega_c})$ (with corresponding energies 0, ω_h, ω_c, and $\omega_h + \omega_c$). From here, we see that the ground state $|00\rangle$ is the most occupied state and the excited state $|11\rangle$ is the least. Thus, the only possibility to extract work from the system via swap is to transpose $|01\rangle \leftrightarrow |10\rangle$ providing that $e^{-\beta_h \omega_h} > e^{-\beta_c \omega_c}$ and $\omega_h > \omega_c$ (i.e., the inversion of population is present). In this case, we achieve the Otto efficiency:

$$\eta_1 = 1 - \frac{\omega_c}{\omega_h}. \tag{5}$$

One may also prove that this is the optimal efficiency in the whole set of unitary operations [60]. The index "1" indicates here a trivial one-dimensional catalyst. Although we mainly focus on efficiency, later we will provide the general formula for the work production [see Eq. (16)].

2-Otto efficiency (two-dimensional catalyst).—Let us now reveal how the efficiency of the process may be increased via the assisted catalyst, which essentially boils down to increasing the hot heat Q_h while keeping the cold one Q_c constant.

From now on, we concentrate solely on disjoint swaps. One may consider an *internal* swap $|ijk\rangle \leftrightarrow |i'j'k\rangle$, that does not affect the state of the catalyst, or the *external* swap $|ijk\rangle \leftrightarrow |i'j'k'\rangle$, with the change in the catalyst state. Clearly, the protocol based solely on internal swaps satisfies the cyclicity at the price of trivializing the problem. Thus, we consider at least one external swap of the type $|ijk\rangle \leftrightarrow |i'j'k'\rangle$. Now, let us label the initial set of occupation probabilities by $\vec{p}_l = (p_1^{(l)}, p_2^{(l)}, p_3^{(l)}, p_4^{(l)})$, for $l = 1$, 2 representing two different states of the catalyst, such that $\vec{p}_1 = p\,\vec{p}_0$ and $\vec{p}_2 = (1-p)\,\vec{p}_0$, where $p \in [0, 1]$ describes the state of the catalyst. The final state of the system (after the permutation) is labeled by $\vec{s}_l = (s_1^{(l)}, s_2^{(l)}, s_3^{(l)}, s_4^{(l)})$, such that the cyclicity constraint is given by $\sum_i p_i^{(l)} = \sum_i s_i^{(l)}$.

Then, let us consider a protocol with only one external swap. We label it by $i \leftrightarrow j$, when the ith state from the first block is swapped with the jth state from the second one. For example, a swap $1 \leftrightarrow 3$ results with a set of occupation probabilities: $\vec{s}_1 = (\mathbf{p_3^{(2)}}, p_2^{(1)}, p_3^{(1)}, p_4^{(1)})$ and $\vec{s}_2 = (p_1^{(2)}, p_2^{(2)}, \mathbf{p_1^{(1)}}, p_4^{(2)})$. In general, for the $i \leftrightarrow j$ swap, one can show that the heat flow is given by

$$Q_{h,c} = \left(\varepsilon_i^{h,c} - \varepsilon_j^{h,c}\right)\left(p_i^{(1)} - p_j^{(2)}\right), \tag{6}$$

where $\varepsilon_i^{h,c}$ are the corresponding energies of the hot or cold TLS associated with the ith state. However, one can easily show that to satisfy the cyclicity condition, i.e., $\sum_i p_i^{(l)} = \sum_i s_i^{(l)}$, the equality $p_i^{(1)} = p_j^{(2)}$ has to be obeyed, which consequently results in no heat and work flow at all. The same reasoning is true for the process with three external swaps, since there is no difference between the catalyst states, and the three-swap process is equivalent to the one-swap process.

As a conclusion, we see that the only advantage that we can get from the presence of the catalyst is for a process with two external swaps. Let us then consider two disjoint swaps: $i \leftrightarrow j$ and $n \leftrightarrow m$. From this, we get a formula for the heat flow:

$$Q_k = \left(\varepsilon_i^k - \varepsilon_j^k\right)\left(p_i^{(1)} - p_j^{(2)}\right) + \left(\varepsilon_n^k - \varepsilon_m^k\right)\left(p_n^{(1)} - p_m^{(2)}\right), \tag{7}$$

and the cyclicity condition translates to the relation $p_i^{(1)} + p_n^{(1)} = p_j^{(2)} + p_m^{(2)}$, such that

$$\delta p \equiv p_i^{(1)} - p_j^{(2)} = -\left(p_n^{(1)} - p_m^{(2)}\right). \tag{8}$$

Finally, we have

$$Q_k = (\varepsilon_i^k + \varepsilon_m^k - \varepsilon_j^k - \varepsilon_n^k)\delta p. \tag{9}$$

Then, to maximize the efficiency, one has to increase the hot heat flow and decrease the cold one. This can be achieved by putting $i = m = 3$ and $j = 2$, $n = 1$. In accordance, we get

$$Q_h = 2\omega_h \delta p, \qquad Q_c = -\omega_c \delta p, \tag{10}$$

which results in the so-called "2-Otto" efficiency:

$$\eta_2 = 1 - \frac{\omega_c}{2\omega_h}. \tag{11}$$

d-Otto efficiency (d-dimensional catalyst).—The generalization of the protocol for d-dimensional catalyst is illustrated in Fig. 2. We propose a specific loop of disjoint swaps, such that the cold and hot current is defined as

$$Q_{h,c} = \sum_i \omega_i^{h,c} \delta p_i, \tag{12}$$

where δp_i is the probability difference and $\omega_i^{h,c}$ is the energy difference (for hot or cold subsystem) for the ith swap. Then, since we consider a loop of swaps, such that each swap links the neighboring columns, the cyclicity condition boils down to a simple condition:

$$\delta p_i = \delta p_j \equiv \delta p, \tag{13}$$

for all i and j, corresponding to null net flow of the probability. With this insight, one designs swaps as in Fig. 2 to get the maximal hot heat flow and minimal (negative)

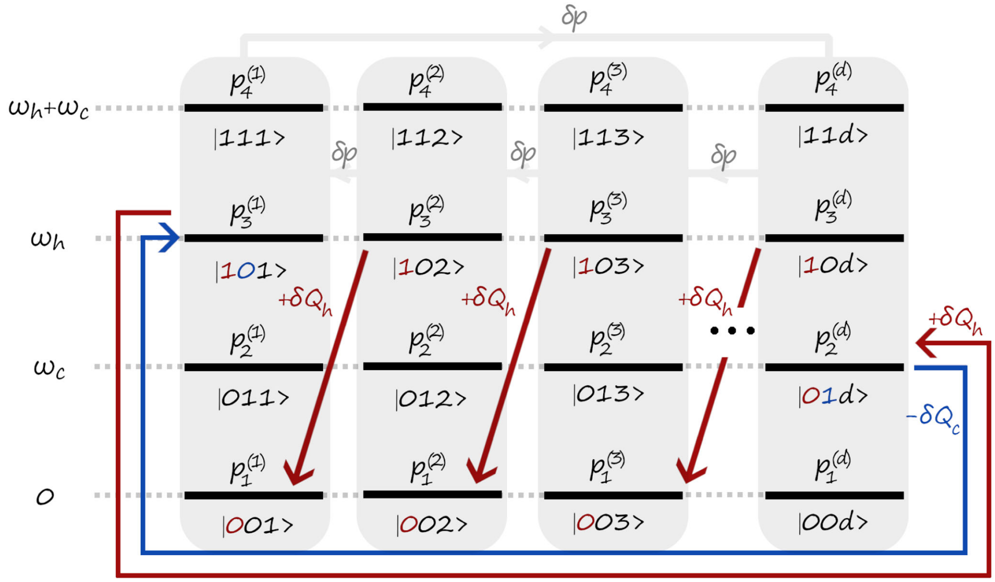

FIG. 2. Graphical representation of disjoint swaps that lead to d-Otto efficiency. The plot represents all the energy levels of the composite system, where $|ijk\rangle \equiv |i\rangle_h |j\rangle_c |k\rangle_s$. Each column represent a kth state of the catalyst, such that the cyclicity condition reflects the conservation of the sum of probabilities within the column. For disjoint swaps, this boils down to the equal flow of the probability δp between the connected columns. Connected levels (via either red or blue arrow) are swapped within the work extraction stage. The red and blue arrows represent the energy changes of hot and cold TLS, respectively, where the up arrow corresponds to increase and down arrow to decrease in energy. The process is designed in such a way that, if $\delta p > 0$, the hot TLS is deexcited in each transposition and the cold TLS is excited in one of the transpositions. For d transpositions, we get the following heat flows: $Q_h = d\delta Q_h = d\omega_h \delta p$ and $Q_c = -\delta Q_c = -\omega_c \delta p$, which implies $\eta = 1 + Q_c/Q_h = 1 - \omega_c/(d\omega_h)$.

cold heat flow, namely,

$$Q_h = d\omega_h \delta p, \qquad Q_c = -\omega_c \delta p, \tag{14}$$

which leads to the generalized efficiency:

$$\eta_d = 1 - \frac{1}{d}\frac{\omega_c}{\omega_h}. \tag{15}$$

Work production and regime of operation.—By solving δp [cf. (8)], we derive the formula for the work production:

$$W_d = Q_h + Q_c = \frac{(d\omega_h - \omega_c)\left(e^{-d\beta_h\omega_h} - e^{-\beta_c\omega_c}\right)}{(1 + e^{-\beta_h\omega_h})(1 + e^{-\beta_c\omega_c}) f_d}, \tag{16}$$

with

$$f_d = \frac{(e^{-d\beta_h\omega_h} - 1)(e^{-\beta_c\omega_c} - 1)}{(1 - e^{-\beta_h\omega_h})^2} + \frac{d(e^{-d\beta_h\omega_h} - e^{-\beta_c\omega_c})(e^{-\beta_h\omega_h} - 1)}{(1 - e^{-\beta_h\omega_h})^2}. \tag{17}$$

According to Eq. (15), the catalyst provides an enhancement in engine efficiency η_d provided the machine works in the engine's mode, i.e., whenever the provided work (16) is positive $W_d > 0$. The condition boils down to the following inequality:

$$\frac{\beta_h}{\beta_c} < \frac{\omega_c}{d\omega_h} < 1, \tag{18}$$

that proves that the engine's efficiency is always smaller than Carnot, i.e., $\eta_d < \eta_c = 1 - \beta_h/\beta_c$.

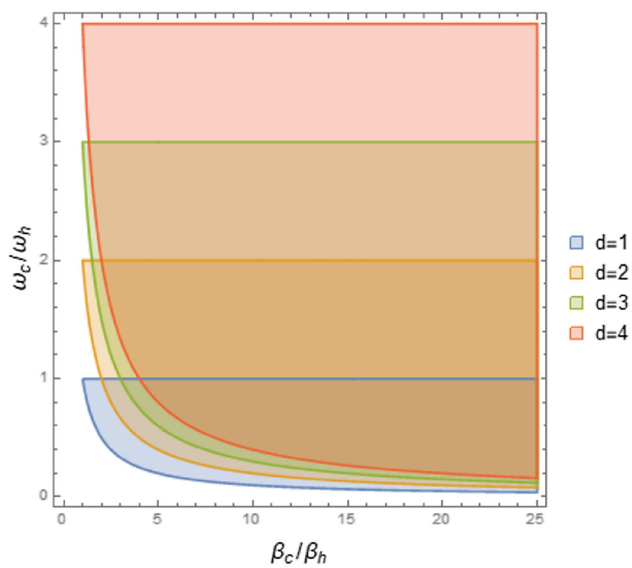

FIG. 3. Regimes of the engine mode. According to inequality (18), the regime of the engine mode (i.e., with $W > 0$) is provided solely by the frequency ratio ω_c/ω_h and temperature ratio β_c/β_h. The graph presents regimes for different dimensions of the catalyst d.

Equivalently, for fixed bath temperatures, we provide the range of all possible dimensions of the catalyst:

$$d \in \left(\frac{\omega_c}{\omega_h}, \frac{\beta_c \omega_c}{\beta_h \omega_h}\right). \tag{19}$$

(A larger range of parameters for which the engine with d-dimensional catalyst is operating was obtained via a more general protocol given in [60]). Figure 3 presents the range of operation of the engine assisted by the d-dimensional catalyst, given by the ratio of frequencies ω_c/ω_h and temperatures β_c/β_h, with extensions due to catalyst visible. Nevertheless, for every $d > 1$, the range for d does not cover the entire range for $d - 1$, so that there exists a regime where only a standard two-stroke Otto engine works (i.e., with $d = 1$), and the catalytic approach is ineffective in improving its efficiency or work production.

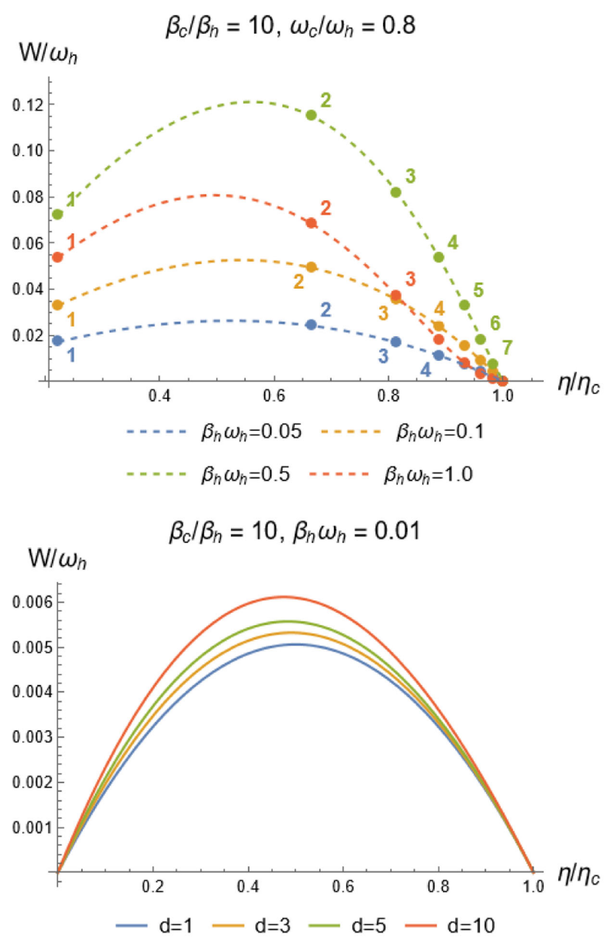

FIG. 4. Efficiency versus work production trade-off. The trade-off for a top panel is explored via changing the dimension of the catalyst d (points on the curve), whereas for a bottom panel via changing the ratio of frequencies ω_c/ω_h. In the top panel, catalytic enhancement is generally observed in the increased efficiency and, particularly, in increased work production. In the bottom panel, the high-temperature limit of the hot bath provides a more favorable trade-off across the full range of operation.

Finally, one may ask, is the catalyst able to enhance also the trade-off between efficiency and work production? In Fig. 4, we provide the positive answer by exploring the trade-off via changing the dimension of the catalyst d or the ratio of frequencies ω_c/ω_h. In particular, one observes that the catalyst can simultaneously increase both the efficiency and power (i.e., the performed work per cycle). Moreover, in the high-temperature limit of the hot bath, by increasing the size of the catalyst, one gets a more preferable efficiency versus power curves in a full range of the engine performance.

Discussion.—This Letter outlines a microscopic heat engine comprised of a pair of two-level systems that completes a thermodynamic cycle in two strokes. Our primary contribution is the formulation of a protocol that surpasses the optimal efficiency of this engine (given by Otto's formula [60]) by incorporating a fine-dimensional catalyst. We have demonstrated that a d-dimensional catalyst results in a generalized d-Otto efficiency (15), which notably exhibits catalytic enhancement even with the smallest two-dimensional catalyst. Additionally, a catalyst extends the engine's operational range and can offer a superior efficiency versus work production trade-off.

The methodology of modifying heat currents via catalysts, studied here for a specific two-stroke engine, can be successfully applied to other thermal machines as well. This opens up avenues for future research in microscopic engines and could contribute to cutting-edge technologies, such as the utilization of thermal machines in quantum computing (e.g., by applying them for the qubit resetting [66]).

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