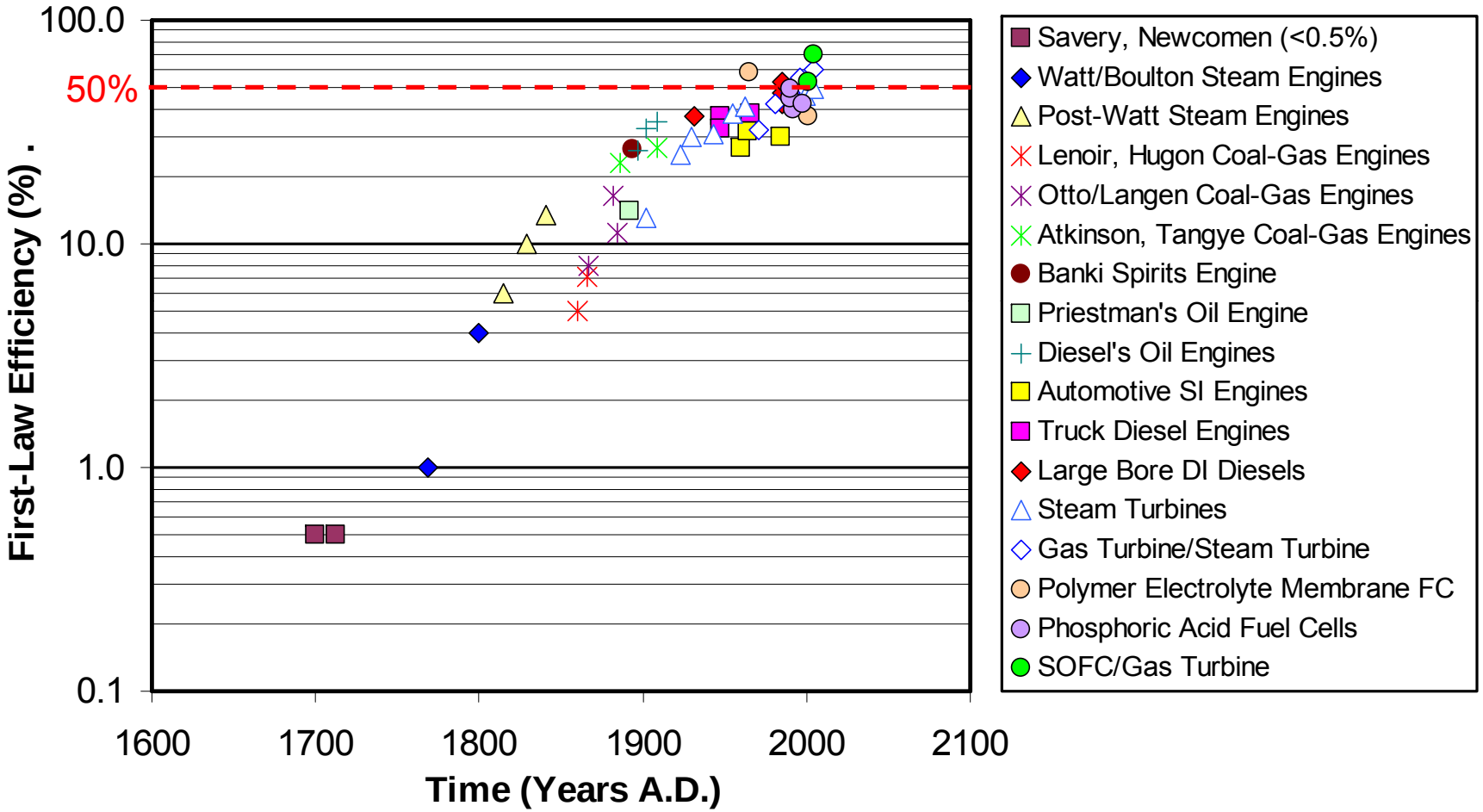
Remarks on the Efficiency Potential of Chemical Engines

Chris F. Edwards

Kwee Yan Teh, Shannon Miller, Matthew Svrcek, Sankaran Ramakrishnan, and Adam Simpson

Advanced Energy Systems Laboratory
Department of Mechanical Engineering
Stanford University

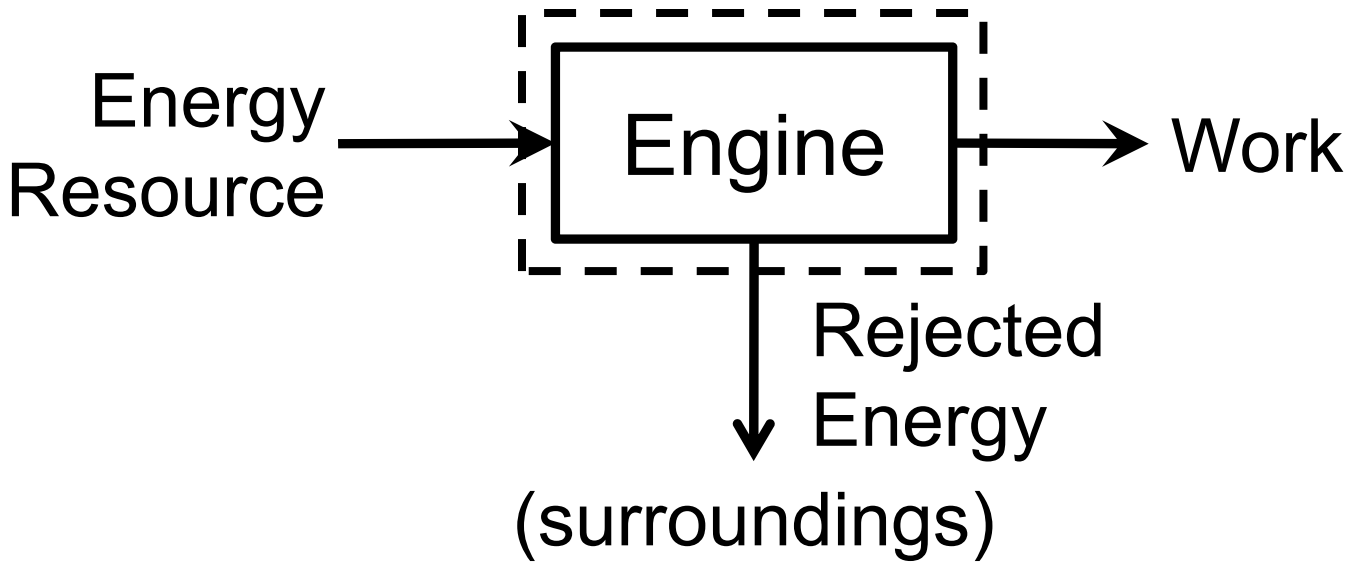
Fuel Conversion Efficiency of Engines



After three centuries of development, combined-cycle efficiency just exceeds 50%, simple-cycle remains below.

Engines

- <u>All</u> engines have three essential features:
  - they produce work (by definition)
  - they require a resource (1st Law)
  - they reject energy to surroundings (2nd Law)



Efficiency Limits

- There are <u>only</u> four ways to transfer energy:
  - work (entropy-free transfer of energy)
  - heat (energy transfer due to ΔT)
  - matter (internal and external energy)
  - radiation (non-thermal)
- These four ways determine the most basic classification of an engine (energy in, entropy out).
- It is the combined *resource* and *surroundings* that ultimately limit the efficiency of an engine. That limit is given by the resource's *exergy*.

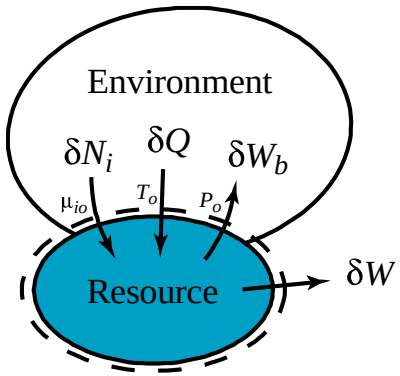
Chemical Exergy of Some Fuels

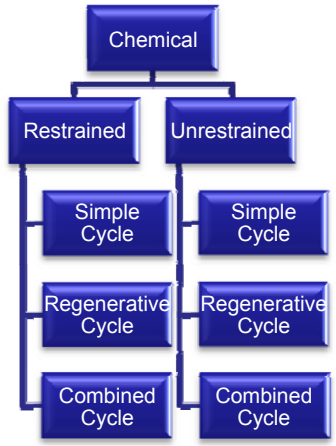
Fuel Species+	Chemical Formula	Chem. Exergy† MJ per fuel kmol	Chem. Exergy† MJ per fuel kg	$\Delta H°$ Reaction* MJ per fuel kmol	$\Delta H°$ Reaction* MJ per fuel kg	$\Delta G°$ Reaction* MJ per fuel kmol	$\Delta G°$ Reaction* MJ per fuel kg	$\Delta S°$ Reaction* kJ/K per fuel kmol	$\Delta S°$ Reaction* kJ/K per fuel kg	Exergy to LHV Ratio
Methane	CH4	832	51.9	-803	-50.0	-801	-49.9	-5.2	-0.33	1.037
Methanol	CH3OH	722	22.5	-676	-21.1	-691	-21.6	50.4	1.57	1.068
Carbon Monoxide	CO	275	9.8	-283	-10.1	-254	-9.1	-98.2	-3.51	0.971
Acetylene	C2H2	1267	48.7	-1257	-48.3	-1226	-47.1	-104.6	-4.02	1.008
Ethylene	C2H4	1361	48.5	-1323	-47.2	-1316	-46.9	-25.2	-0.90	1.029
Ethane	C2H6	1497	49.8	-1429	-47.5	-1447	-48.1	60.5	2.01	1.048
Ethanol	C2H5OH	1363	29.6	-1278	-27.7	-1313	-28.5	117.7	2.56	1.067
Propylene	C3H6	2001	47.6	-1926	-45.8	-1937	-46.0	36.6	0.87	1.039
Propane	C3H8	2151	48.8	-2043	-46.3	-2082	-47.2	129.2	2.93	1.053
Butadiene	C4H6	2500	46.2	-2410	-44.5	-2421	-44.7	36.9	0.68	1.038
i-Butene	C4H8	2644	47.1	-2524	-45.0	-2560	-45.6	120.2	2.14	1.047
i-Butane	C4H10	2800	48.2	-2648	-45.6	-2712	-46.7	214.4	3.69	1.058
n-Butane	C4H10	2805	48.3	-2657	-45.7	-2717	-46.7	200.0	3.44	1.056
n-Pentane	C5H12	3460	48.0	-3272	-45.3	-3353	-46.5	271.3	3.76	1.057
i-Pentane	C5H12	3454	47.9	-3265	-45.2	-3347	-46.4	277.0	3.84	1.058
Benzene	C6H6	3299	42.2	-3169	-40.6	-3190	-40.8	69.4	0.89	1.041
n-Heptane	C7H16	4769	47.6	-4501	-44.9	-4625	-46.2	415.0	4.14	1.060
i-Octane	C8H18	5422	47.5	-5100	-44.7	-5259	-46.0	531.4	4.65	1.063
n-Octane	C8H18	5424	47.5	-5116	-44.8	-5261	-46.1	487.1	4.26	1.060
Jet-A	C12H23	7670	45.8	-7253	-43.4	-7440	-44.5	626.4	3.74	1.057
Hydrogen	H2	236	117.2	-242	-120.0	-225	-111.6	-56.2	-27.88	0.977

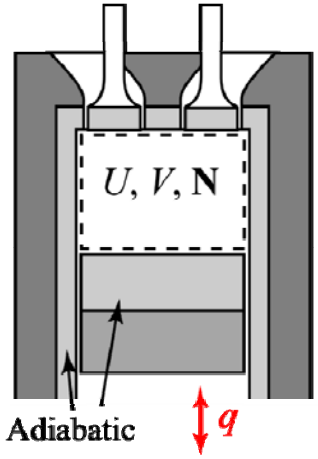
+All species taken as ideal gases. †Environment taken as: 25°C, 1 bar, 363 ppm CO_2, 2% H_2O, 20.48% O_2, balance N_2 .
*Reaction with stoichiometric air at 25°C, 1 bar. All products present as ideal gases, including water.

Fuel Conversion Efficiency potential (maximum first-law efficiency based on LHV) of most fuels is ~100%.

Spanning Exergy to Engines



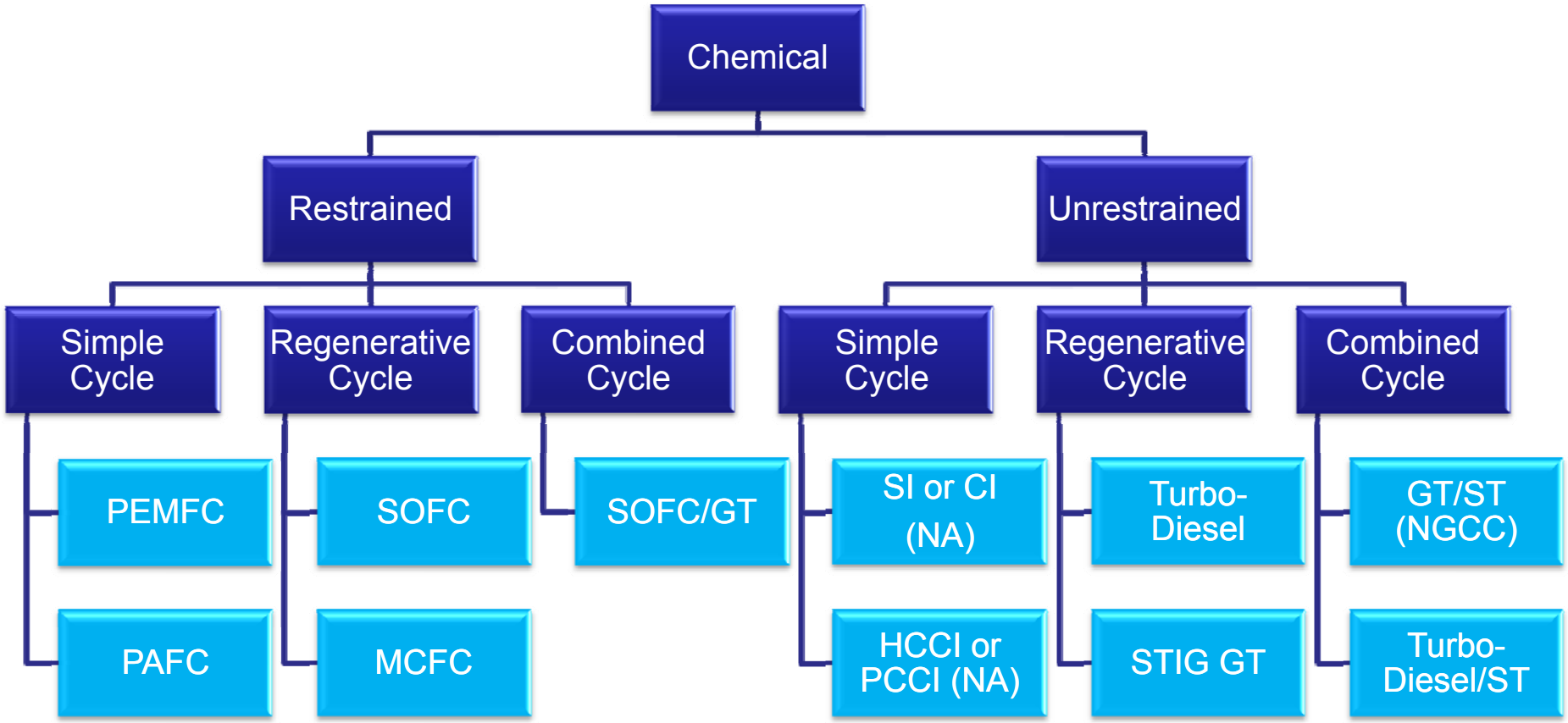




Exergy ⟶ Classification ⟶ Architecture ⟶ Engines

Classification and *Architecture* can be useful intermediates for understanding how to bridge from exergy to engines.

Classification



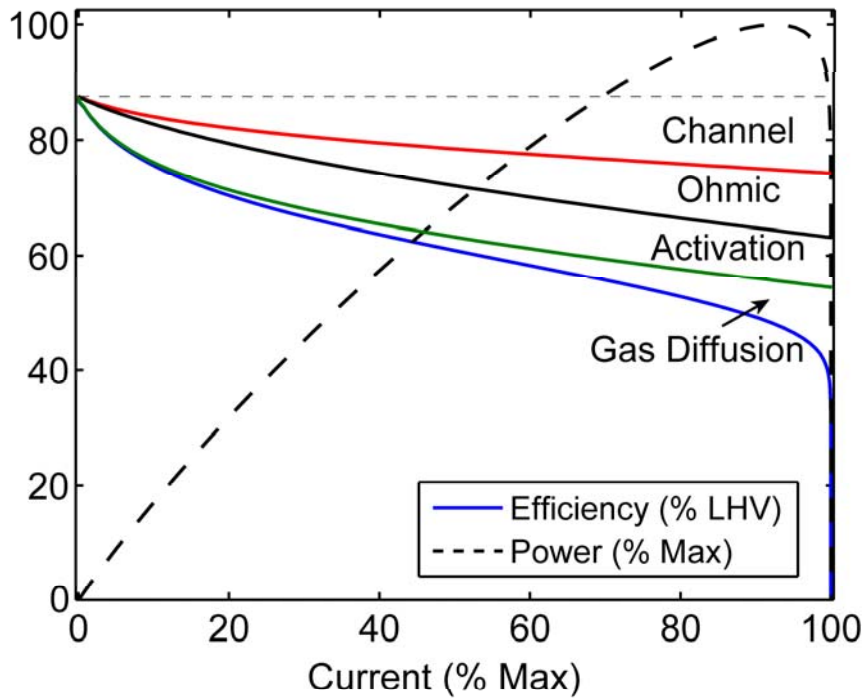
Classification can be useful for understanding limitations associated with choices about key processes.

Two Approaches to Reaction

- Unrestrained
  - Reactants are initially internally restrained, i.e., frozen in chemical non-equilibrium (e.g. combustion, fuel reforming).
  - Internal restraint is released, allowing reaction to proceed.
  - Reaction “stops” when equilibrium is achieved or kinetics are so slow as to be negligible (frozen again).
  - Inherently irreversible.
- Restrained
  - Reactants are initially externally restrained, i.e., in chemical equilibrium (e.g. electrochemistry, solution chemistry).
  - External restraints are changed, allowing reaction to proceed.
  - Never stops; always dynamically balanced.
  - Reversible only in the limit of infinitesimal rate and constrained chemical pathway (chemical reversibility).

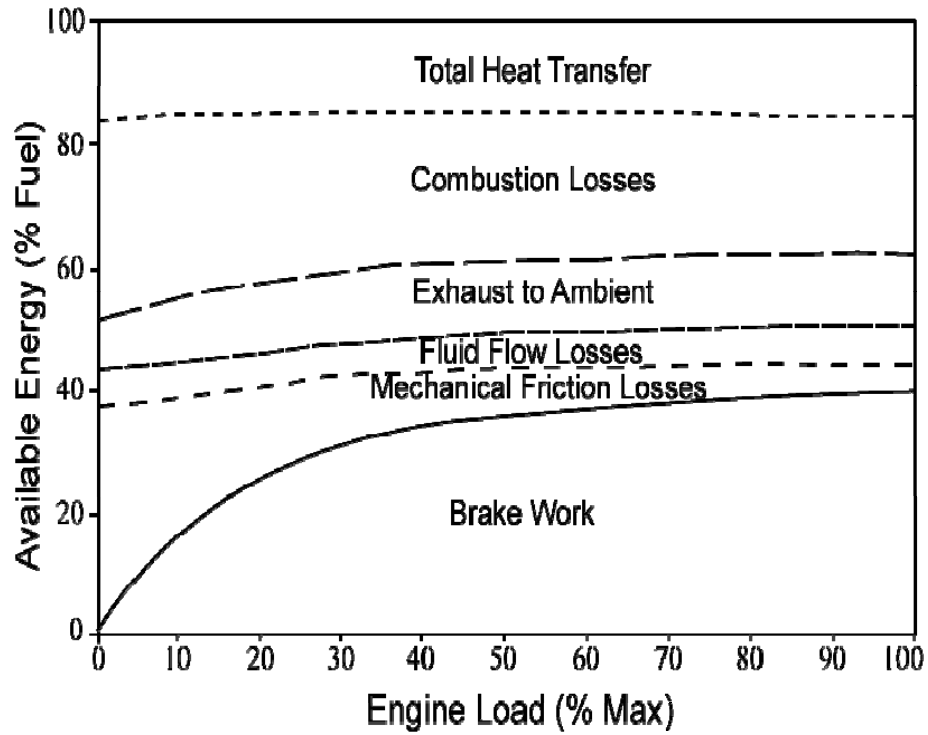
Restrained vs. Unrestrained

Restrained (SOFC)



- Efficiency declines with load
- Irreversibility reduced via facile kinetics (reaction and transport)

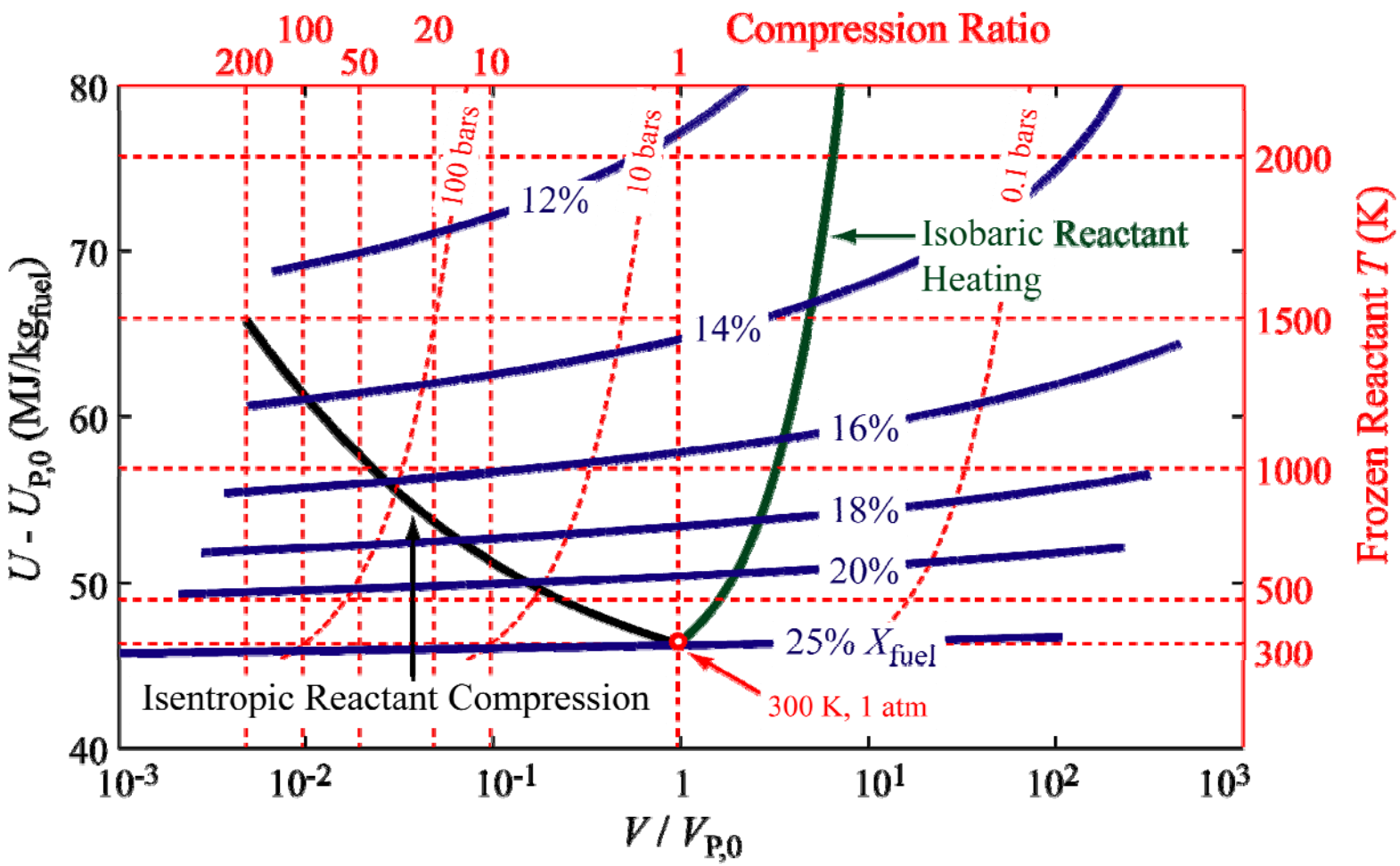
Unrestrained (DI Diesel*)



- Efficiency improves with load
- Irreversibility reduced by reaction at extreme states

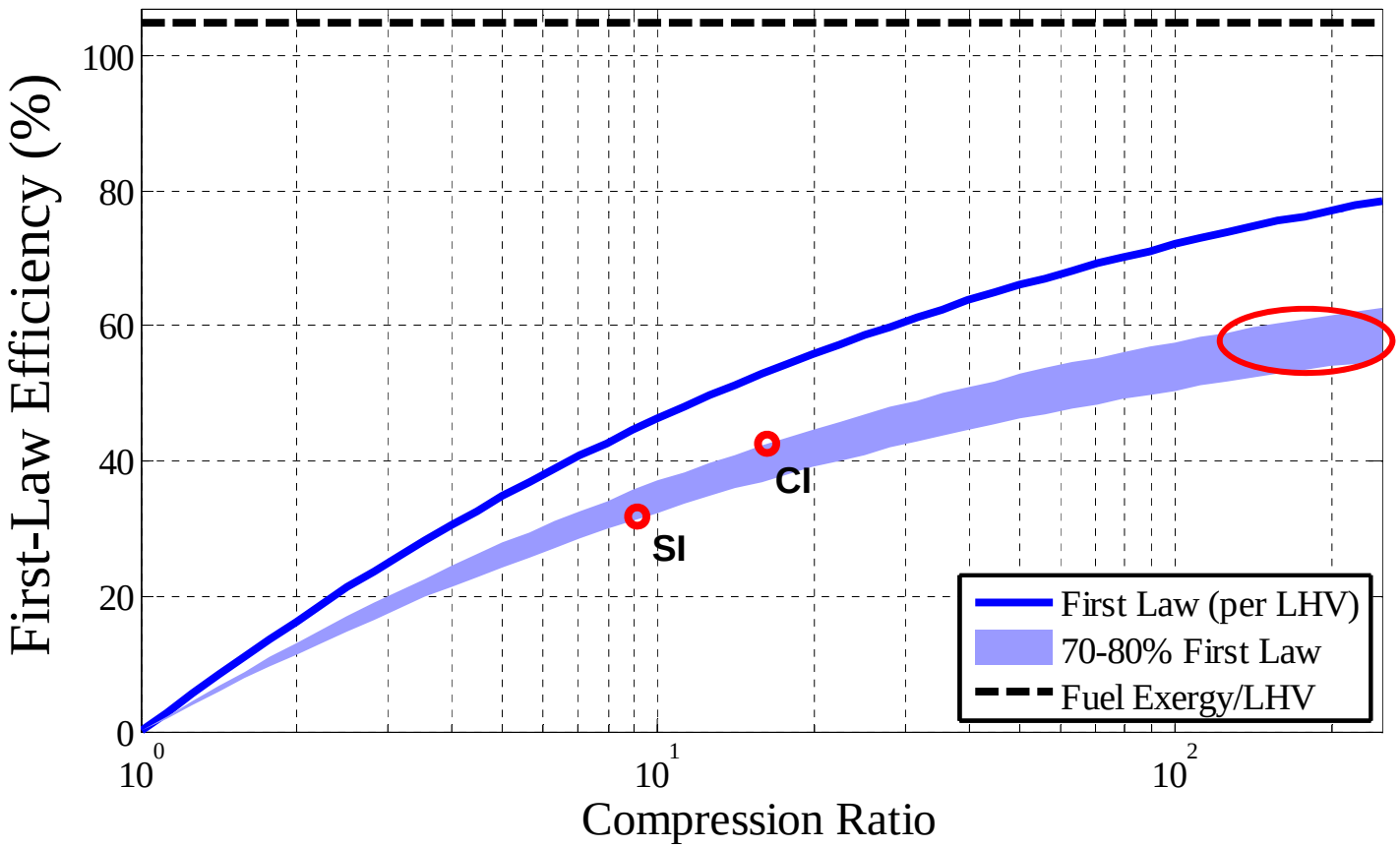
* After Primus, et al. “Proceedings of International Symposium on Diagnostics and Modeling of Combustion in Reciprocating Engines, (1985) p.529-538.

Exergy Destruction via Reaction



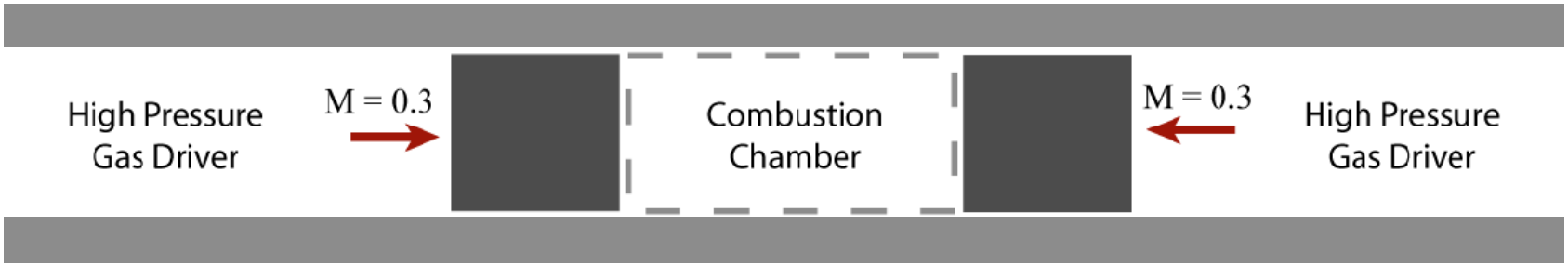
Stoichiometric propane/air mixture modeled as ideal gases.
Includes the effects of variable specific heats, reaction, & dissociation.

Efficiency Potential of the Reactive Otto Cycle Architecture



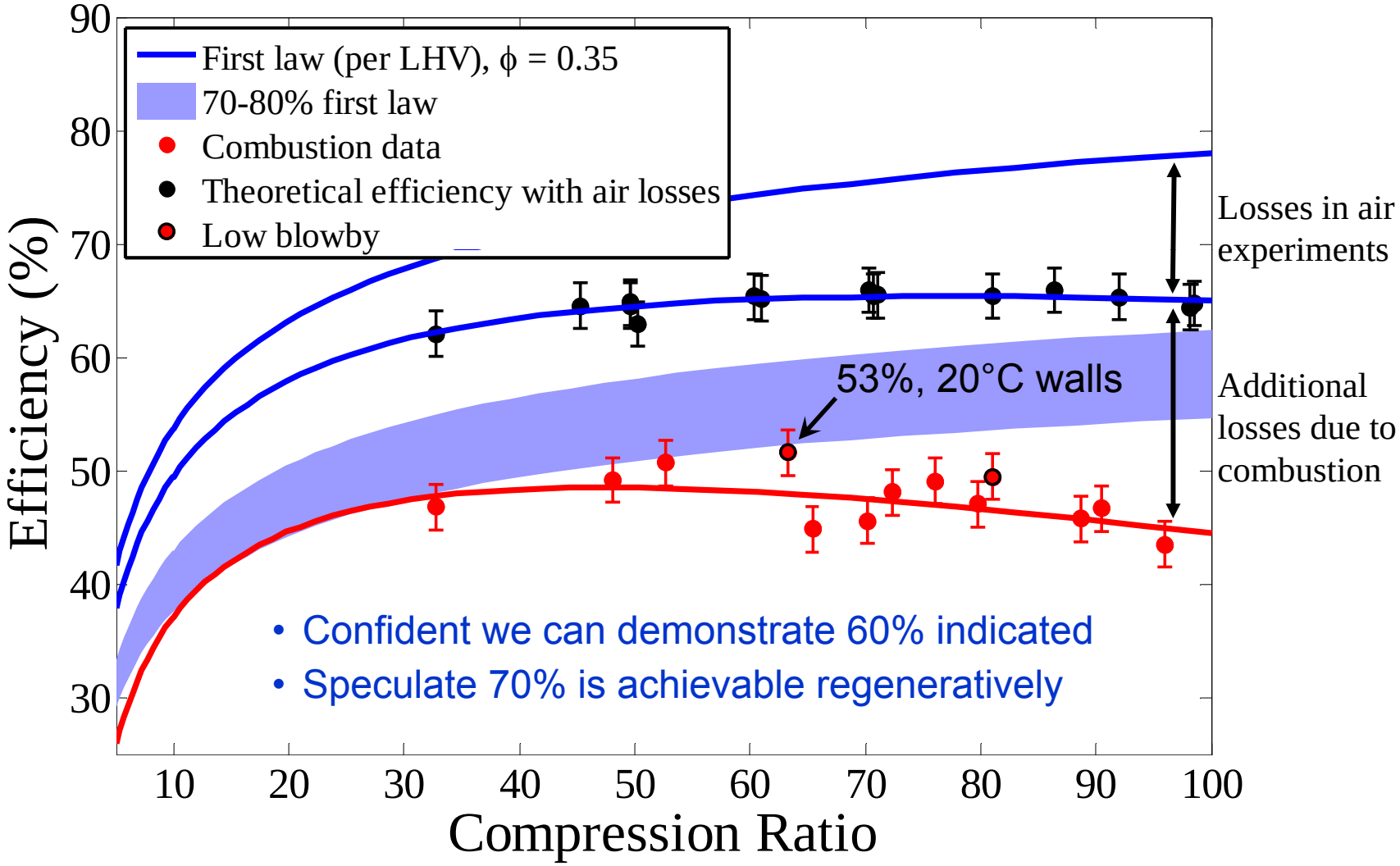
Stoichiometric propane/air

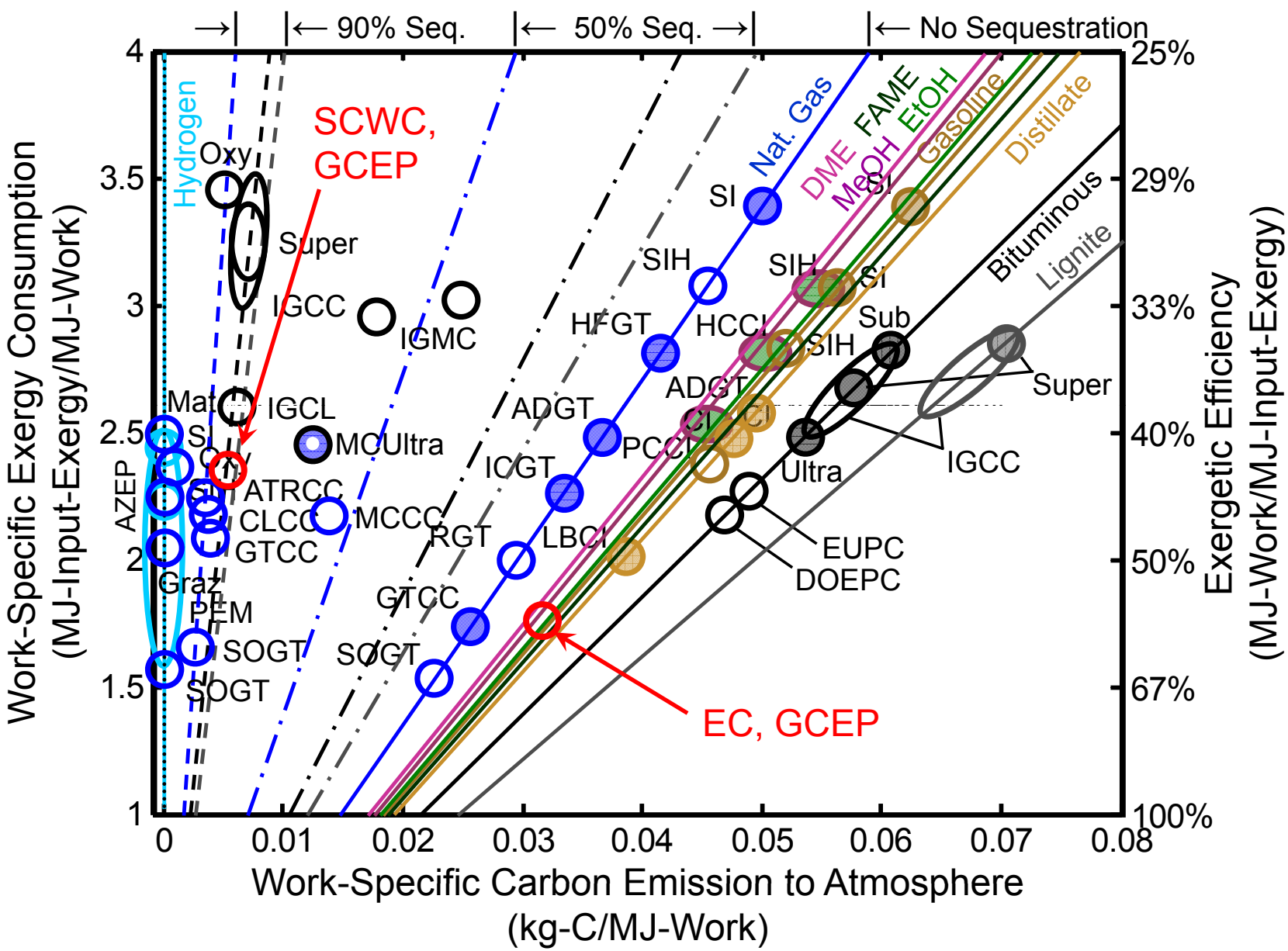
Extreme Compression



- High compression ratio, ~100:1
- Multiple pistons (balanced forces, ~unity aspect ratio)
- High speeds, M~0.3 (reduced time for heat transfer)
  - air at 300 K, speed of sound ~ 350 m/s → 100 m/s
  - for reference: 3000 RPM and 90 mm stroke → 9 m/s

Extreme Compression: Initial Results





→| |← 90% Seq. |← 50% Seq. →| |← No Sequestration
Work-Specific Exergy Consumption
(MJ-Input-Exergy/MJ-Work)
Exergetic Efficiency
(MJ-Work/MJ-Input-Exergy)
Work-Specific Carbon Emission to Atmosphere
(kg-C/MJ-Work)
SCWC,
GCEP
EC, GCEP
Hydrogen
Oxy
Super
IGCC
IGMC
IGCL
MCUltra
ATRCC
CLCC
GTCC
MCCC
Mat
Si
AZEP
Graz
PEM
SOGT
SOGT
SOGT
GTCC
RGT
ICGT
ADGT
HFGT
SIH
SI
Nat. Gas
DME
FAME
MeOH
EtOH
Gasoline
Distillate
Bituminous
Lignite
HCCI
SIH
SI
SIH
Sub
Super
IGCC
Ultra
EUPC
DOEPC
ADGT
PCCI
LBCI

Take-Home Messages (1 of 2)

- Despite three centuries of effort, engine efficiency remains well below theoretical limits (resource exergy)—often by more than a factor of two.
- Misconceptions about what ultimately limits engine efficiency (e.g., Carnot) are sometimes to blame.
- Working in the space between the exergy limit and real engines, we have found the ideas of *classification* and *architecture* to be useful.
- Our approach is to use the principles of optimal control to identify the most efficient architecture for any given set of allowable devices, resources, and environment.
- For chemical engines, a key to understanding is whether the architecture uses *restrained* or *unrestrained* reaction.

Take-Home Messages (2 of 2)

- Irreversibility in restrained reaction engines can be reduced by improving kinetics. To date, the only examples of restrained reaction engines are electrochemical (i.e., fuel cells).
- Irreversibility in unrestrained reaction engines can be reduced by reaction at states of high energy density (*extreme-states principle*).
- For simple-cycle engines, we believe that architectures capable of delivering 60% first-law efficiency are possible.
- For regenerative engines, we believe a systematic approach to identifying optimal architectures can be developed. We speculate that such engines are capable of 70% first-law efficiency.
- For combined-cycle engines, we speculate that a systematic approach is again possible and can lead to the development of engines with first-law efficiencies in excess of 80%.