Chemical Reaction Waste Heat Recovery for Process Intensification

"Now, in the *second* law of thermodynamics . . ."

Dr. David Vernon
Assistant Professor
Schatz Energy Research Center
Environmental Resources
Engineering Department
Humboldt State University
Arcata, CA

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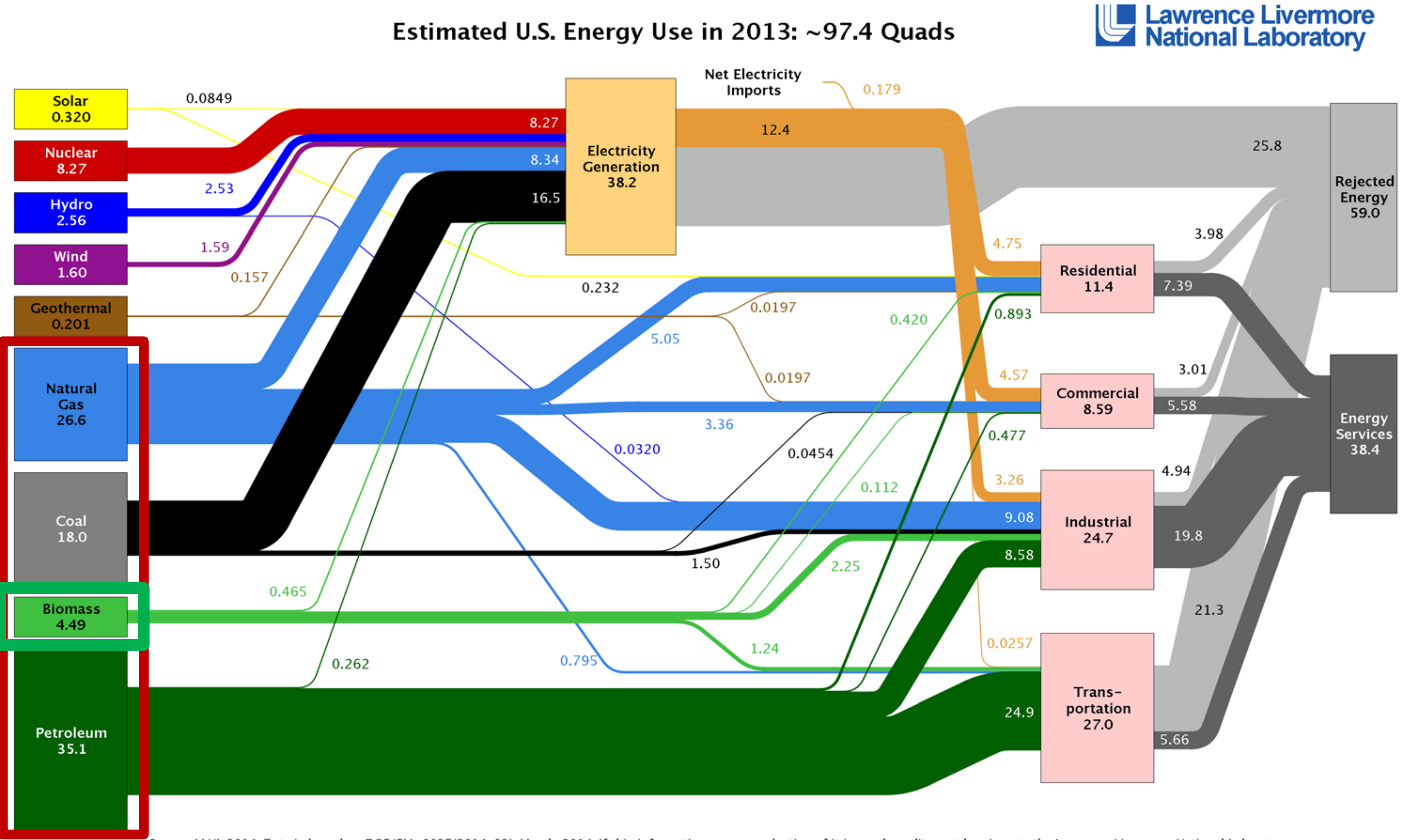
86% of primary energy is chemical energy
4.6% of primary energy from biomass



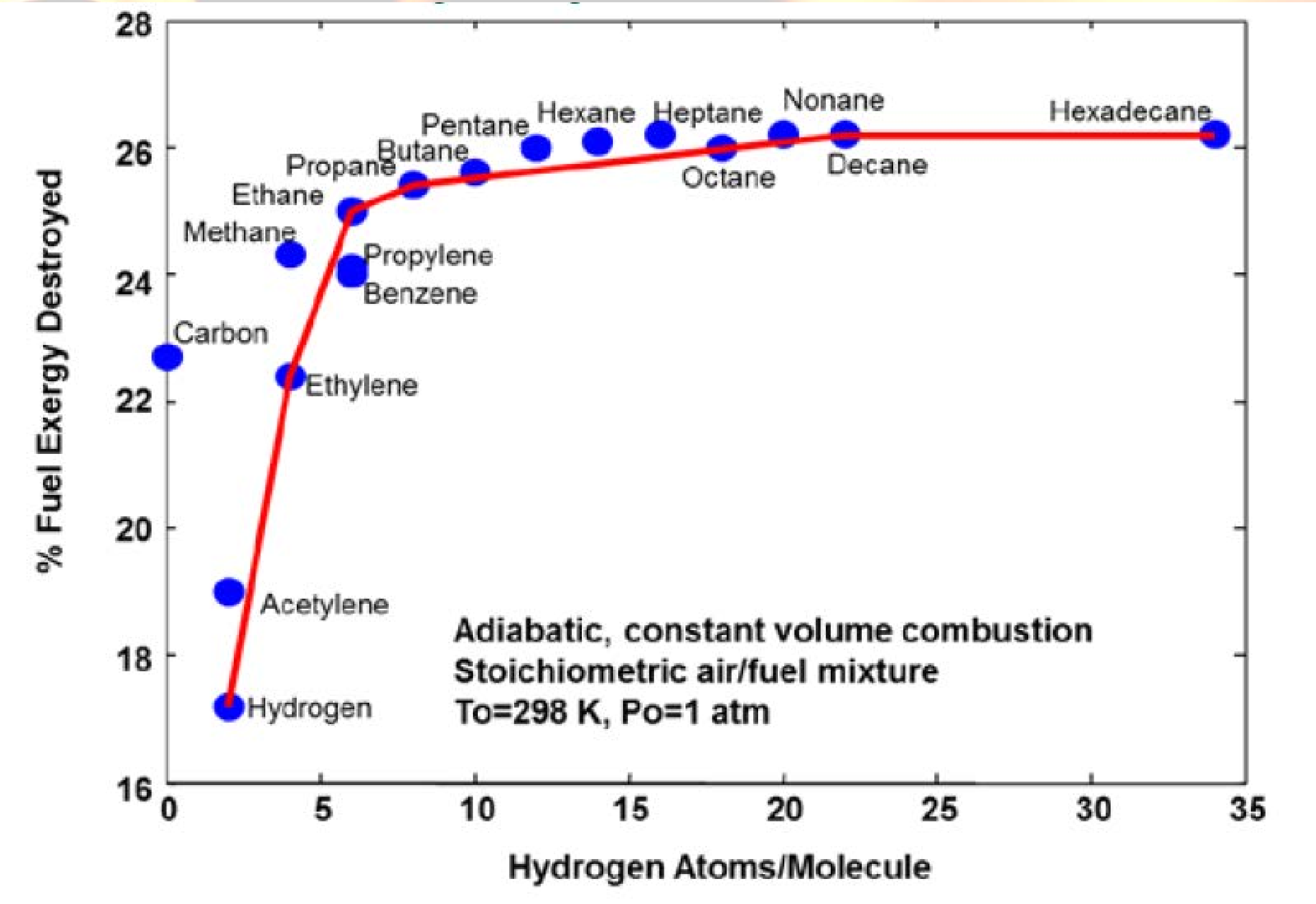
Source: LLNL 2014. Data is based on DOE/EIA-0035(2014-03), March, 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential and commercial sectors 80% for the industrial sector, and 21% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Destruction of Exergy from Waste Heat Rejection

Engine Type	Fraction of Fuel LHV (Fuel Exergy) in Exhaust	Fraction of Fuel LHV (Fuel Exergy) in Coolant
Spark Ignition Automotive	34-45% (8-17%)	17-26% (1-3%)
Diesel Automotive	22-35% (7-15%)	16-35% (1-3%)
Large Stationary (1-17.1 MW, NG)	25-41% (11-21%)	13-17% (1-2%)
Gas Turbine (1-40MW, NG)	45-75% (26-36%)	

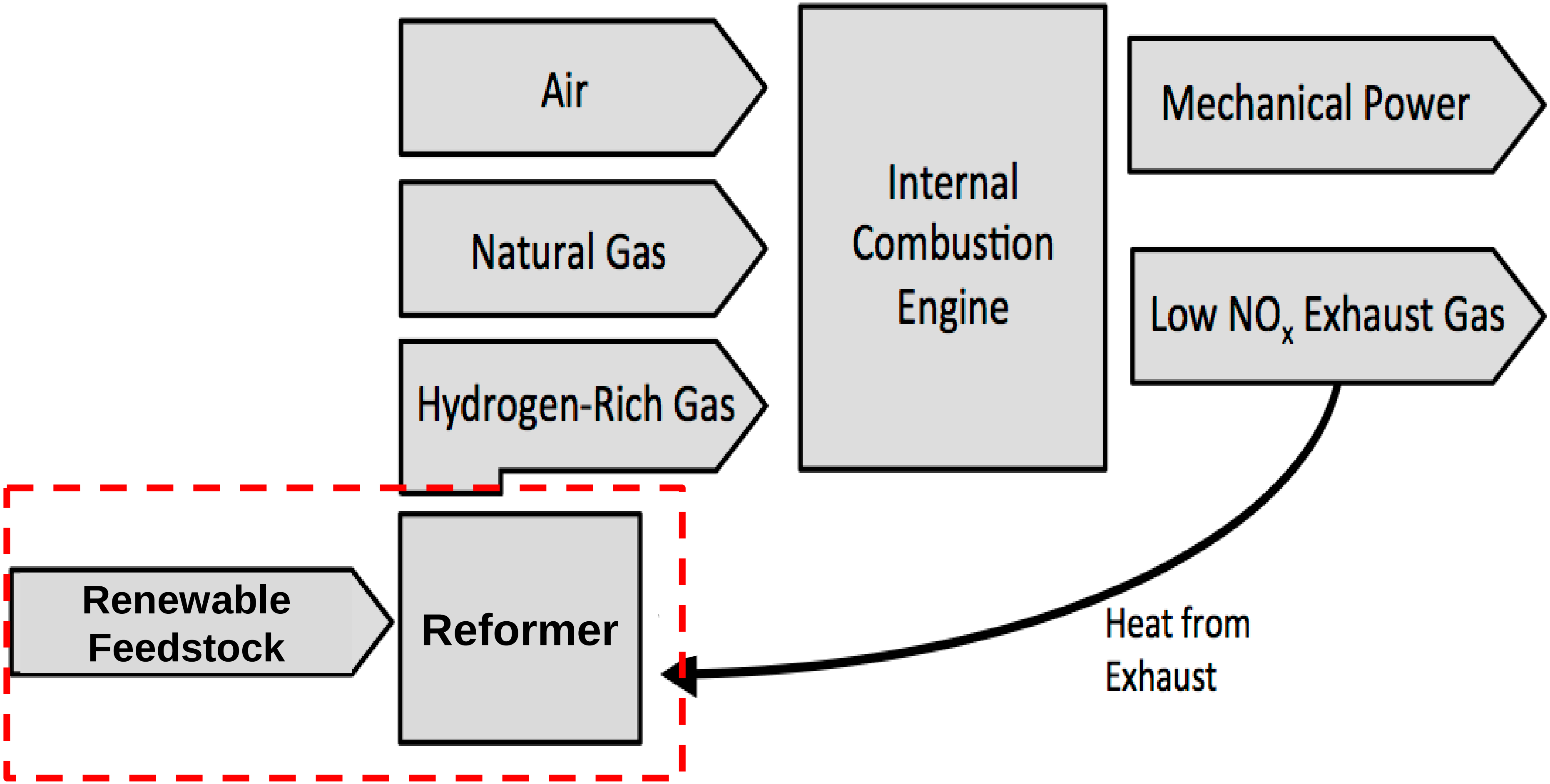
Heywood, “Internal combustion engine fundamentals”, 1989; C.D. Rakopoulos, “Second-law analyses applied to internal combustion engines operation”, 2006; Wagner, “Defining Engine Efficiency Limits”, 2011; Wagner,” Achieving and Demonstrating Vehicle Technologies Engine Fuel Efficiency Milestones”, 2009; Wartsilla Engine Specifications 2013; EPA, Catalog of CHP Technologies, 2008 : J.H. Horlock “Advanced Gas Turbine Cycles: A Brief Review of Power Generation Thermodynamics”, 2003

Combustion Destruction of Fuel Exergy

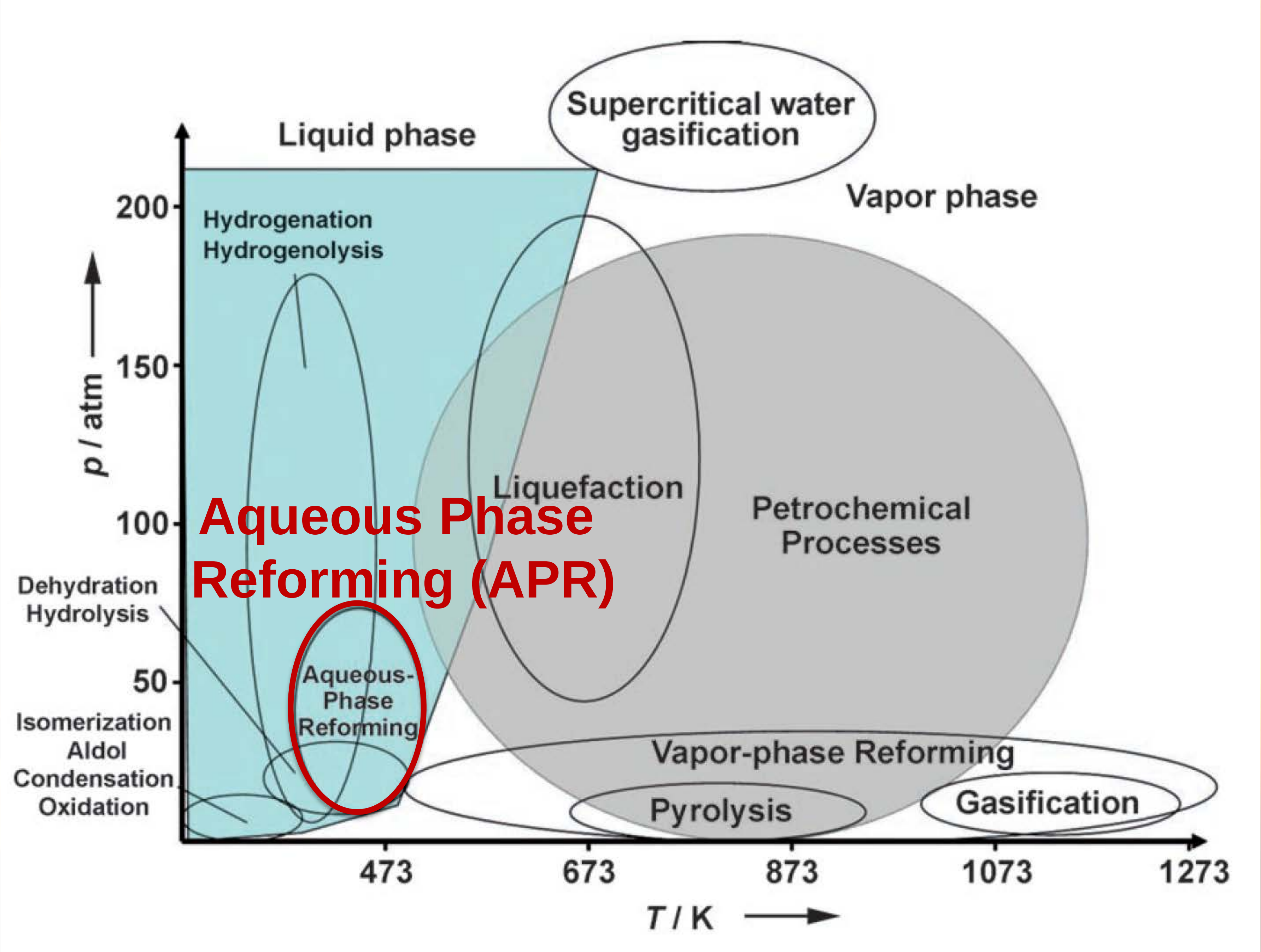


Wagner, “Defining Engine Efficiency Limits”, 2011, Original source Jerry Caton Texas A&M

Chemical Reaction Waste Heat Recovery



Aqueous Phase Reforming (APR)



Chheda et al., Liquid-Phase Catalytic Processing of Biomass-Derived
Oxygenated Hydrocarbons to Fuels and Chemicals, Angew. Chem. Int. Ed. 2007, 46, 7164 – 7183

Why Aqueous Phase Reformation?

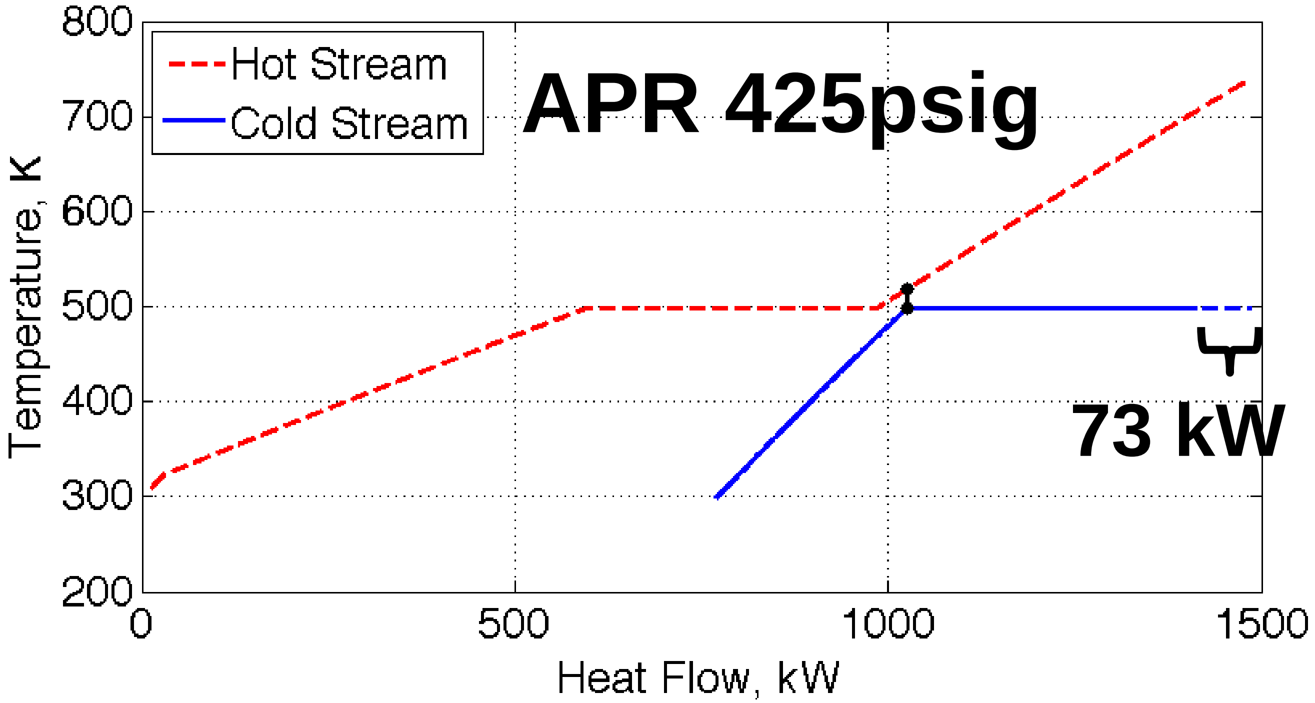
- **Reform renewable plant-derived or waste feedstocks that are not volatile and or are available as dilute aqueous solutions**
- **Lower reaction temperatures compared to gas phase reformation**
  - Increase potential waste heat recovery
  - Reduce cost

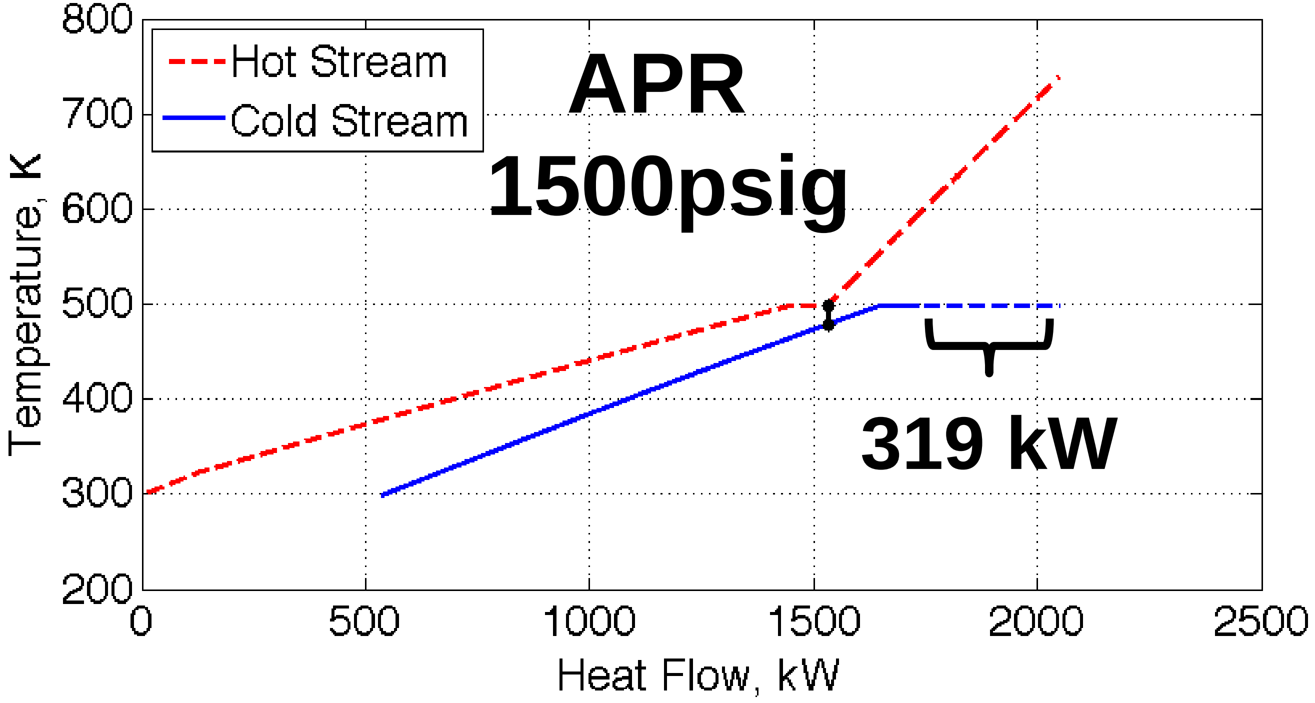
APR Waste Heat Recovery Technology Goals for ICEs

- Replace over 30-100% of required fossil fuel with renewable biomass-derived or waste feedstocks
- Increase overall system efficiency by up to 25%
- Reduce emissions of NO_x by up to 95%, while reducing or maintaining low CO, HC, and PM emissions

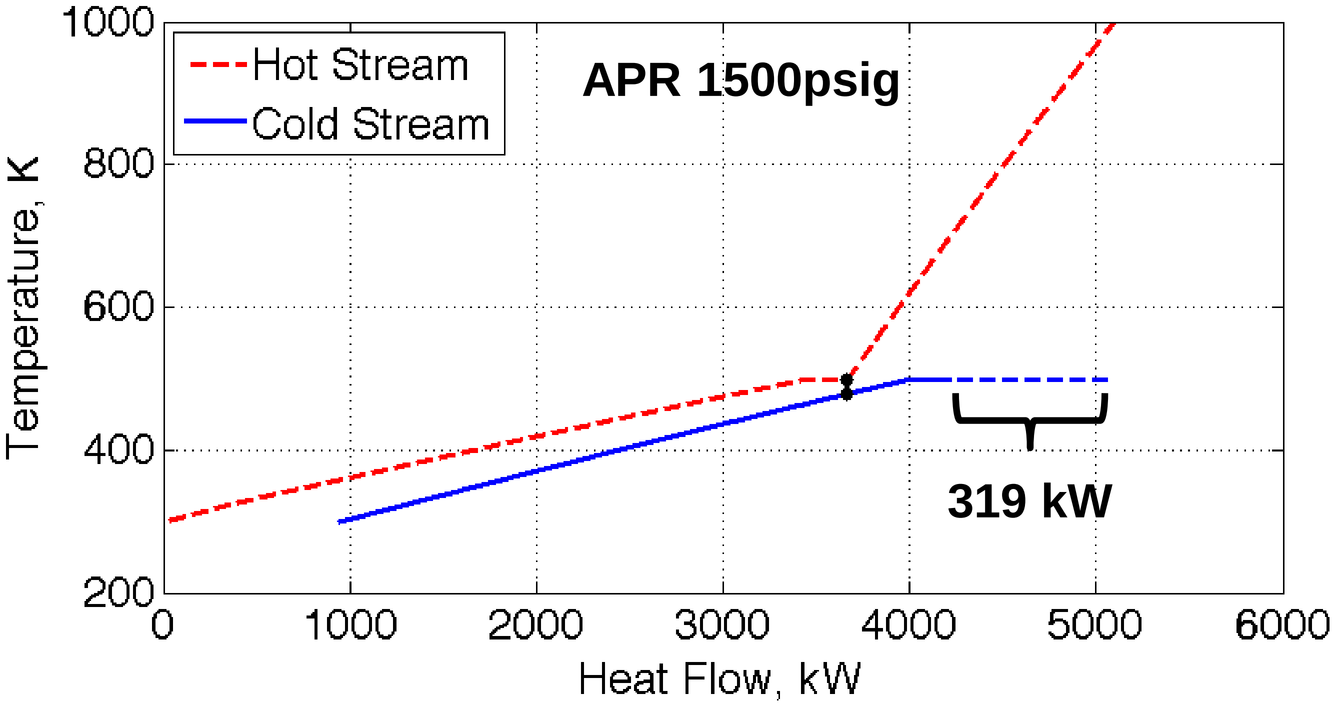
APR Challenges

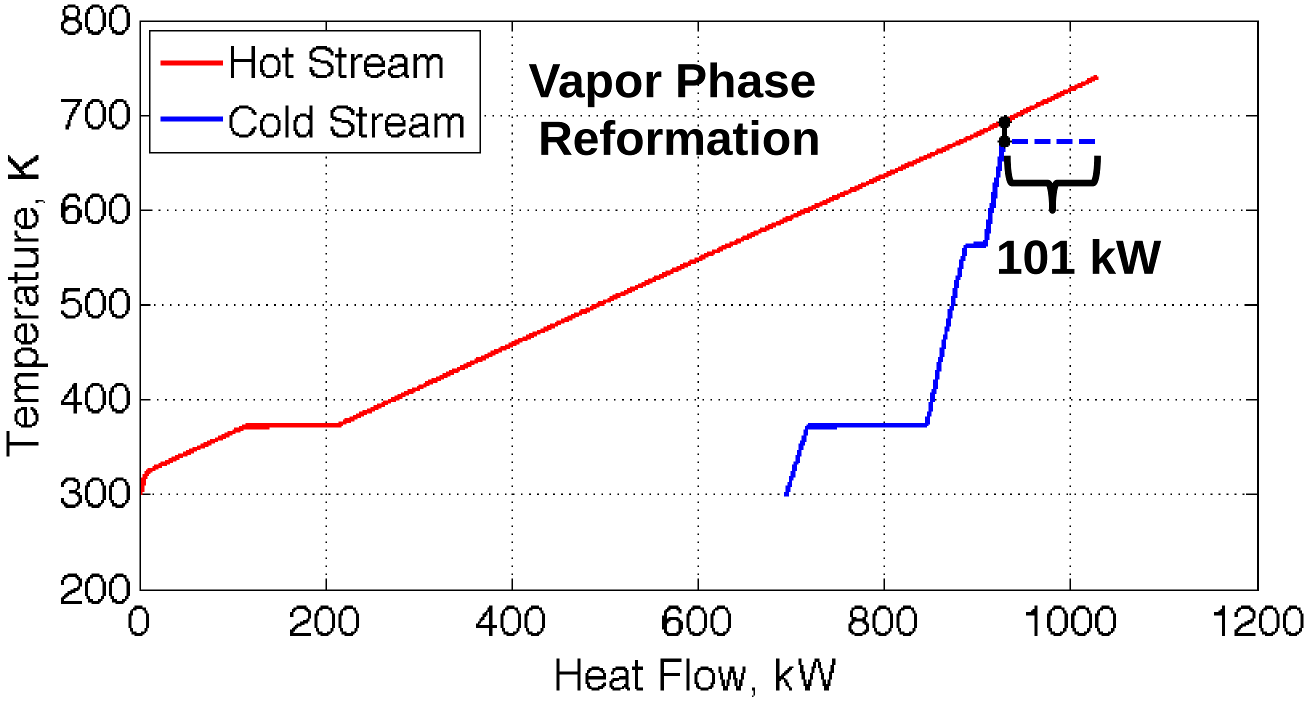
- **Catalysts and reaction kinetics in early stage of understanding**
- **Side products can lead to incomplete conversion**
- **Water evaporation into dry gases consumes a portion of recovered heat**





- **Glycerol Feedstock**
- **APR at 225^{o}C**
- **Caterpillar G3516LE 1.0MW NG engine, $T_{exhaust}$ 467^{o}C**



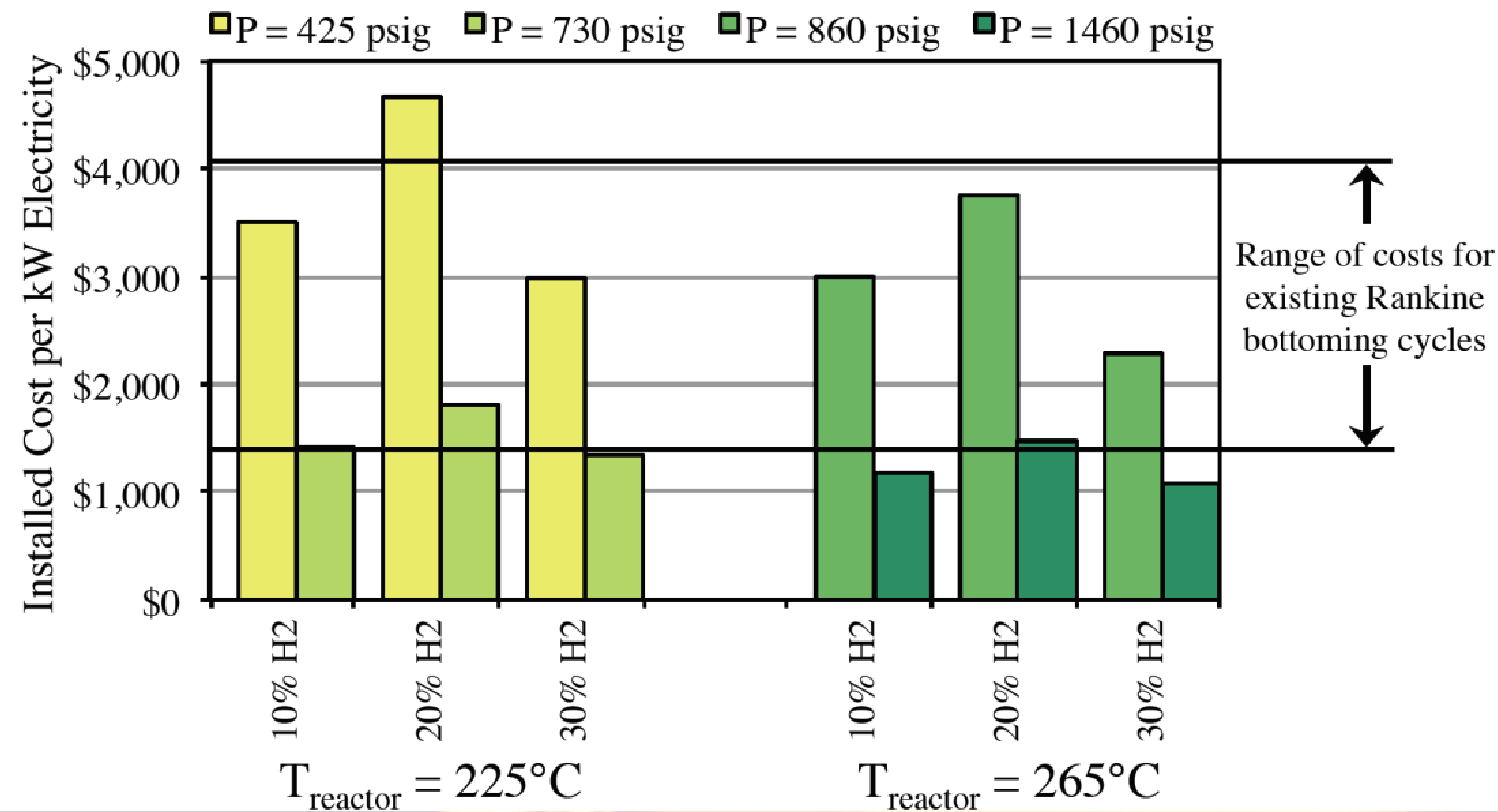


- **Glycerol Feedstock**
- **APR at 225°C**
- **VPR at 400°C**
- **Caterpillar G3516LE 1.0MW engine, $T_{exhaust}$ 467°C**

Pinch Analysis: Fraction of Exhaust Thermal Energy Converted to Chemical Energy

Engines: Caterpillar NG	**VPR 400^{o}C**	**APR 1500psig 225^{o}C**
T_{exh} 873^{o}C (G3615, 1MW shaft, η=32.3%)	33%	43%
T_{exh} 529^{o}C (G3615B, 1.4MW shaft, η=33.8%)	24%	41%
T_{exh} 467^{o}C (G3615LE, 1MW shaft, η=34.4%)	12%	37%

Estimated capital and installation costs of glycerol APR waste heat recovery system per kW of increased electricity production for NG fueled ICEs



Current APR Experiments

- Determine hydrogen production rates at practical temperatures and pressures using in-house synthesized state of the art catalysts
- Measure effluent liquid species (products vs. disposal costs)
- Recirculation to increase conversion and concentrate side products

Future APR Experiments

- Real biomass derived and waste feedstocks, impact of contaminants and pretreatment methods
- Innovative reactor designs, membrane reactor, and integrated heat exchanger reactor
- Near-critical and Supercritical water gasification of effluent for complete conversion

Acknowledgements

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