Intensification of thermochemical processes through autothermal operations

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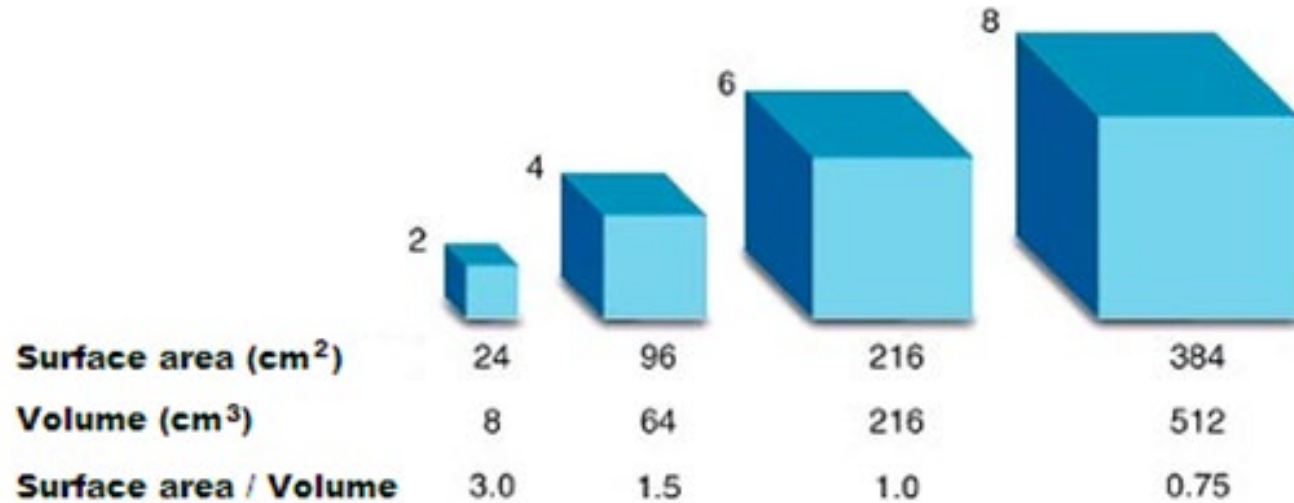
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The importance of surface area-to-volume (A/V) ratio in heat and mass transfer

Volume quickly overtakes surface area as system scales up

A mass transfer example

	2	4	6	8
Surface area (cm²)	24	96	216	384
Volume (cm³)	8	64	216	512
Surface area / Volume	3.0	1.5	1.0	0.75

A Heat Transfer Example

The absorption/release of energy by a (volumetric) chemical reaction must not out pace the heat transfer rate into/out of a reactor is steady operation is to be achieved:

$$\dot{Q}_{hx} > \dot{H}_{rx}$$

$$hA(T_w - T_{rx}) > k_c C_A V \Delta H_{rx}$$

$$(A/V) > k_c C_A \Delta H_{rx}/h(T_w - T_{rx})$$

Assumes tubular reactor of diameter D, length L, fixed diameter-to-length ratio, φ, heat transfer coefficient h, wall and reactor temperatures T_w and T_{rx}, respectively, first order chemical reaction with rate constant k_c, reactant concentration C_A, and enthalpy of reaction ΔH_{rx}.

Minimum A/V ratio and maximum reactor diameter for three distinct chemical processes in tubular reactors

Parameter	Methane Reforming	Fast Pyrolysis	Composting
Temperature	1270°C	500°C	50°C
Reaction rate coefficient	140 s^{-1}	0.094 s^{-1}	1.7 x 10^{-6} s^{-1}
Concentration of reactant	3.8 kg m^{-3}	180 kg m^{-3}	150 kg m^{-3}
Chemical reaction rate, R	532 kg s^{-1} m^{-3}	16.9 kg s^{-1} m^{-3}	2.55x10^{-4} kg s^{-1} m^{-3}
Enthalpy change, ΔH_{rx}	+12.9 MJ kg^{-1}	+1 MJ kg^{-1}	-8.5 MJ kg^{-1}
Energy absorption/release rate, $\dot{H}_{rx}$	6.9x10^6 kW m^{-3}	1.7x10^4 kW m^{-3}	-2.2 kW m^{-3}
Heat transfer coefficient, h	1000 W m^{-2} K^{-1}	100 W m^{-2} K^{-1}	24 W m^{-2} K^{-1}
Temperature gradient, ΔT	200 K	400 K	25 K
Heat transfer rate	200.0 kW m^{-2}	40.0 kW m^{-2}	0.6 kW m^{-2}
Minimum A/V ratio	35,000 m^{-1}	425 m^{-1}	3.6 m^{-1}
Maximum reactor diameter	0.11 mm	9.4 mm	1100 mm

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Reactor throughput for heat transfer limited vs chemical kinetically limited processes

Heat transfer limited process

$$R_{hx}(mol\ s^{-1}) = h\pi DL(T_w - T_{rx}) = h(T_w - T_{rx})\varphi\pi D^2$$

Chemical reaction limited process

$$R_{rx}(mol\ s^{-1}) = k_c C_A \frac{\pi}{4}D^2 L = k_c C_A \varphi \frac{\pi}{4}D^3$$

Assumes tubular reactor of diameter D, length L, fixed diameter-to-length ratio, φ, heat transfer coefficient h, first order chemical reaction with rate constant k_c, and reactant concentration C_A
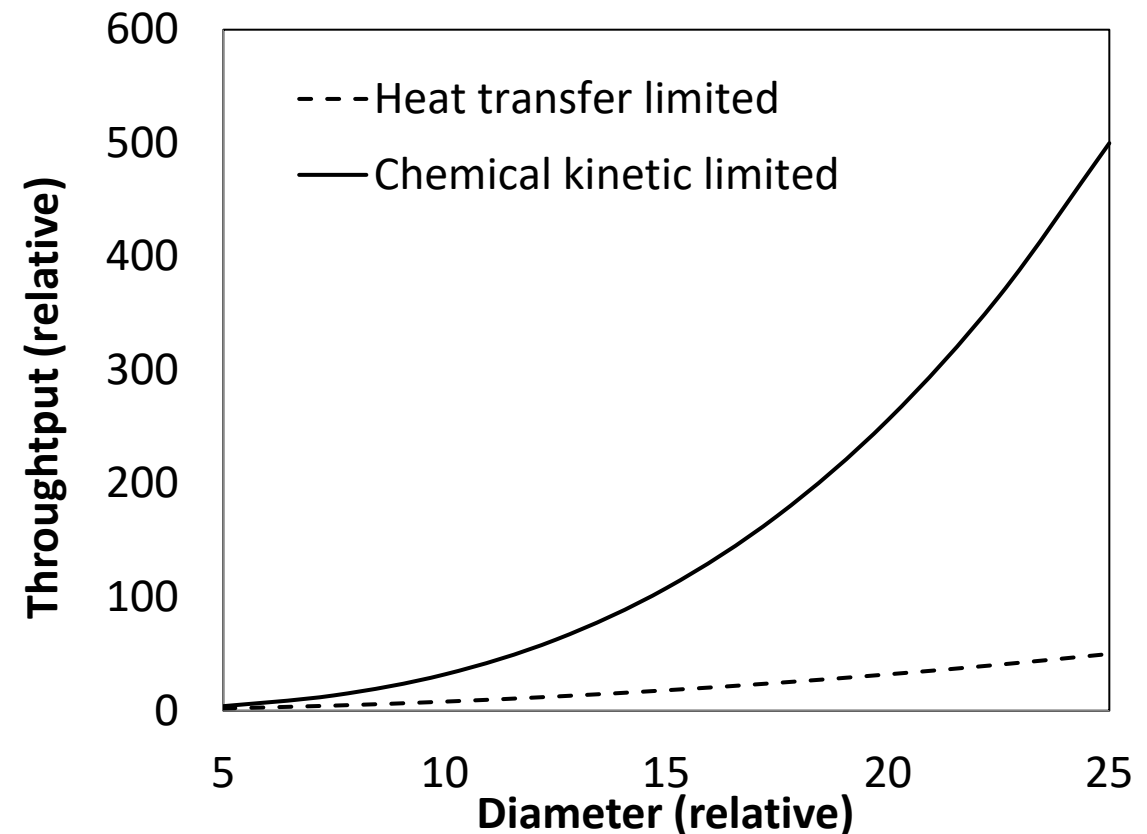
Process Intensification Scales Linearly with the Diameter of an Autothermal Reactor

Process Intensification, I

$$I = \frac{R_{rx}}{R_{hx}} = \frac{k_c C_A \varphi(\frac{\pi}{4}) D^3 |\Delta H_{rx}|}{h(T_w - T_{rx})\varphi \pi D^2} = \frac{k_c C_A |\Delta H_{rx}|}{4h(T_w - T_{rx})} D$$

Assumes tubular reactor of diameter D, length L, fixed diameter-to-length ratio, φ, heat transfer coefficient h, wall and reactor temperatures T_w and T_{rx}, respectively, first order chemical reaction with rate constant k_c, reactant concentration C_A, and enthalpy of reaction ΔH_{rx}.
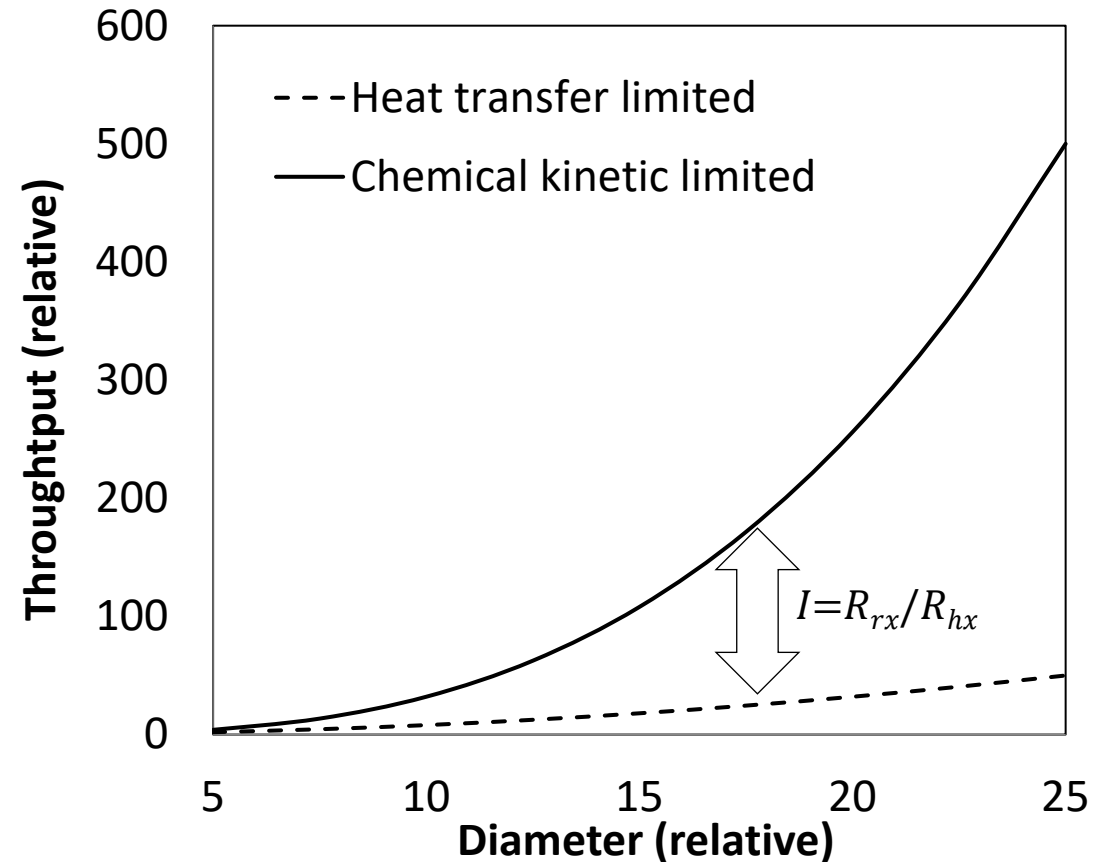
These improvements in process intensification are expected whether a thermal coupling reaction replaces indirect or direct heat transfer and regardless of the heat exchanger configuration.

Heat transfer to/from reactor perimeter
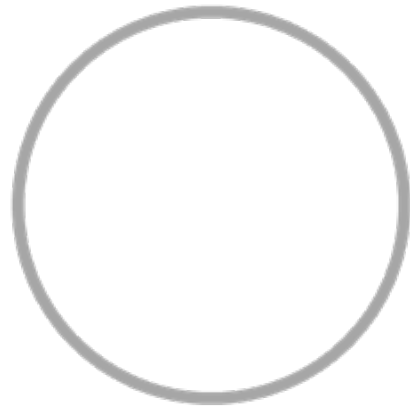
Heat transfer to/from tube array

Heat transfer to/from granular heat carrier

$$\dot{Q} \sim 2\pi D L$$
$$\dot{Q} \sim D^2$$

$$\dot{Q} \sim (A_S/tube)(tubes/A_c)\,\pi D^2$$
$$\dot{Q} \sim D^2$$
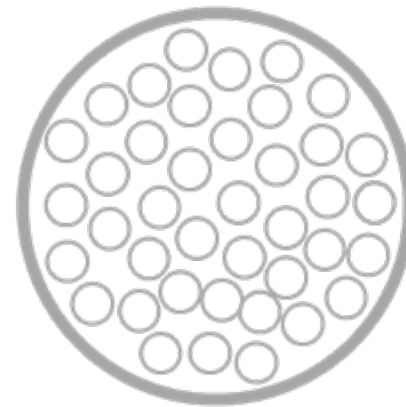
$$\dot{Q} \sim j_p (C_p \Delta T)\,\pi D^2$$
$$\dot{Q} \sim D^2$$

L: reactor length; $A_S/tube$: surface area of a heat transfer tube in the reactor; $tubes/A_c$: number of tubes per cross-sectional area of the reactor; j_p: mass flux of granular heat carrier entering the reactor; $C_p\Delta T$: sensible energy per unit mass of granular heat carrier).

Cost scales linearly with throughput for a reactor limited by heat transfer while a reactor limited by chemical kinetics scales as the 2/3 power of reactor throughput

- <u>Heat transfer limited process:</u> Since both cost and throughput scale as the square of the reactor diameter, cost of a reactor increases linearly with throughput

- <u>Chemical kinetic limited process:</u> Since cost scales as the square of reactor diameter while throughput increases as the cube of reactor diameter, cost increases as the two-thirds power of throughput, in accordance with the classical economy of scale principle
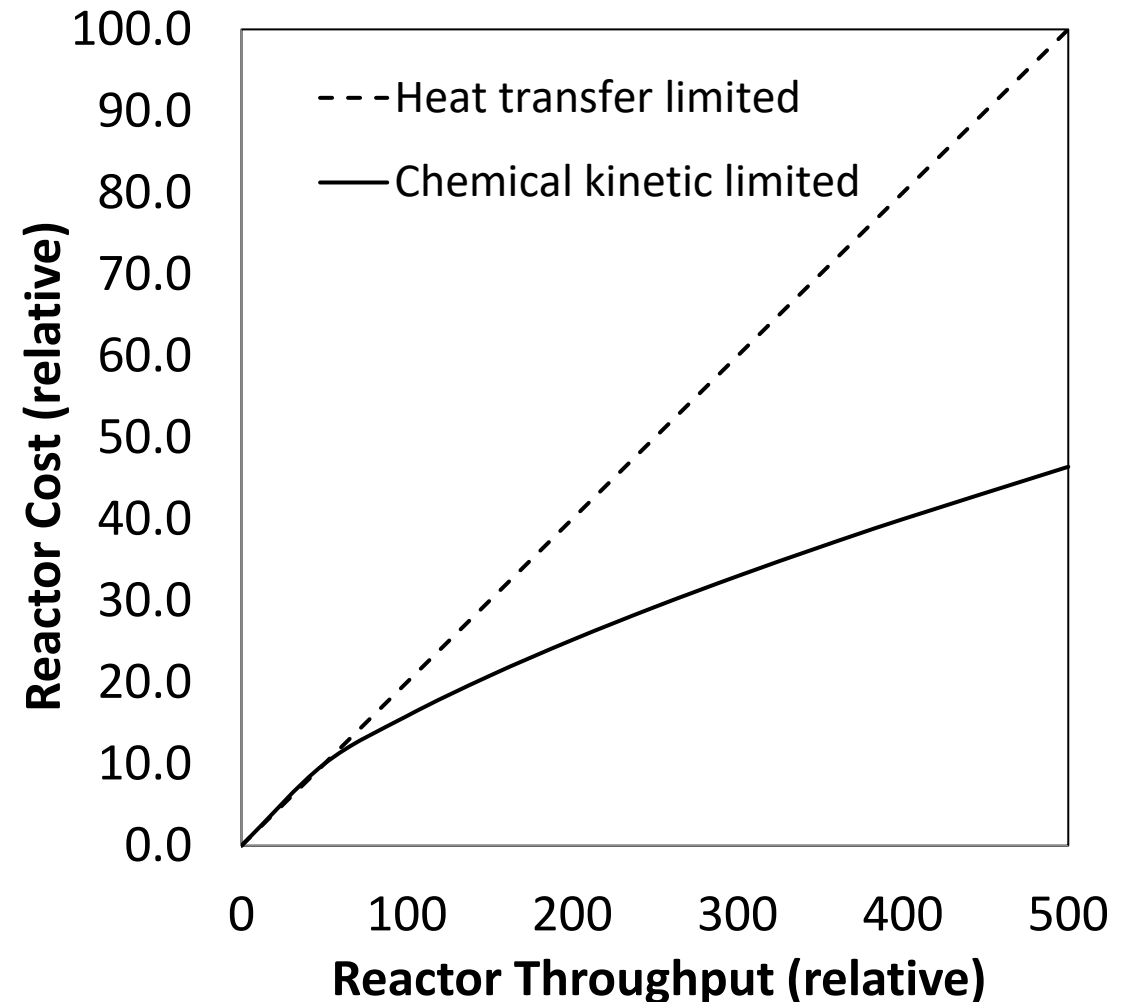
Implications of autothermal processing

- Elimination of heat exchange simplifies reactor design

- Capital and operating costs is eliminated for ancillary equipment associated with heat exchangers including pumps, blowers, and conveyers for liquid, gaseous, and solid heat transfer media

- Dramatic increase in reactor throughput by eliminating heat transfer bottleneck that characterizes many chemical processes

- Several fold greater throughputs than comparably sized reactors that depend on heat transfer for thermal management

Novel Examples of Directly Coupled Autothermal Reaction Systems

- Oxidative dehydrogenation of alkanes

- Oxidative dehydrogenation of methanol to formaldehyde

- Autothermal reduction of metals and limestone

- Dehydration of methanol (CH_3OH) to dimethyl ether (CH_3OCH_3)

- (Biological) composting of wet biomass

- Methanol dehydration to dimethyl ether

- Cracking of methane to produce hydrogen with reduced CO_2 emissions

- Autothermal electrolysis of water

- Hydrothermal processing of biomass at Iowa State University (see Habeeb Odebiyi's oral presentation on Thursday afternoon)

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Autothermal fast pyrolysis of biomass at Iowa State University

Fluidized bed pyrolyzer assures good mixing of air and biomass
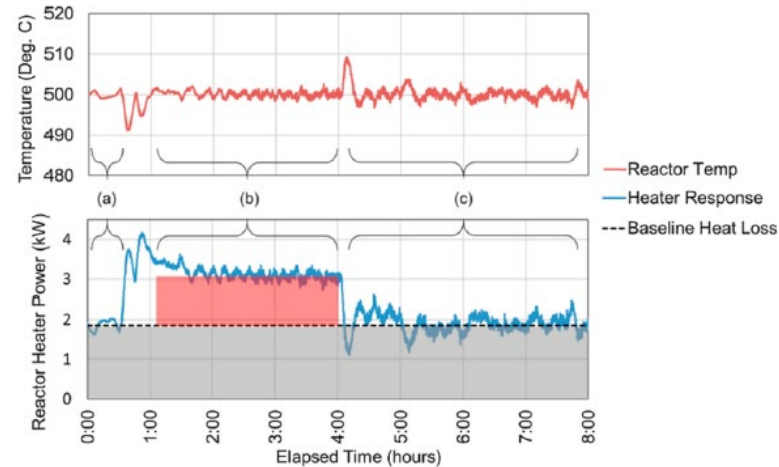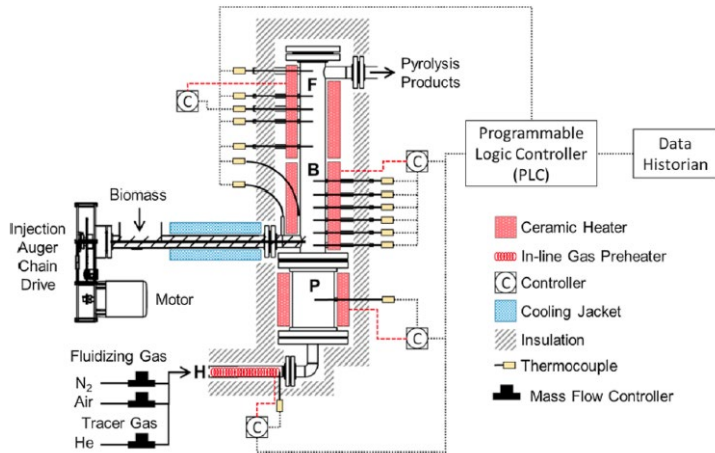
Autothermal operation achieved at 500⁰C for equivalence ratios as low as 0.07

Most of the enthalpy for pyrolysis comes from char oxidation
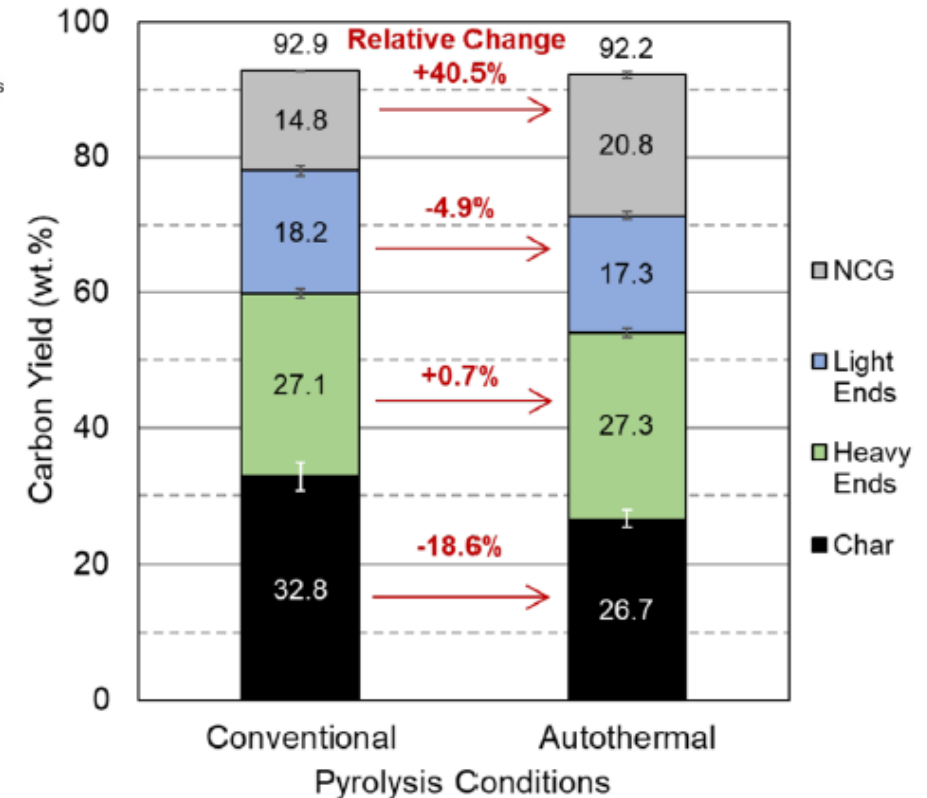
Thermal oxo-degradation (TOD) of waste plastics at Iowa State University

Pyrolysis of HDPE at 600°C almost autothermal at 4% equivalence ratio
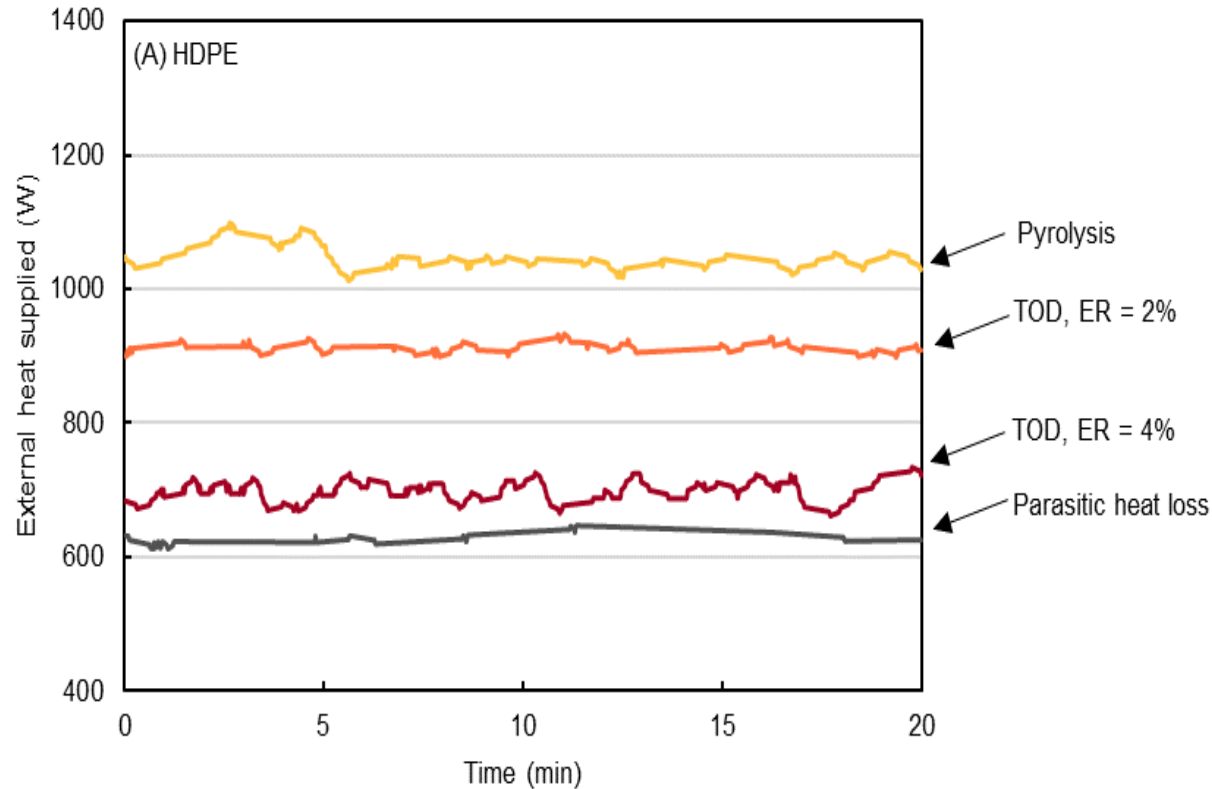
Wax + liquid yield almost unchanged
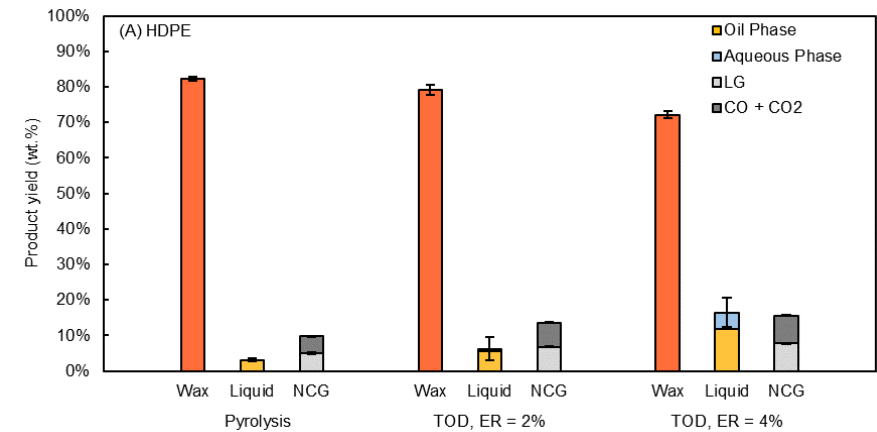
Oil composition almost unchanged
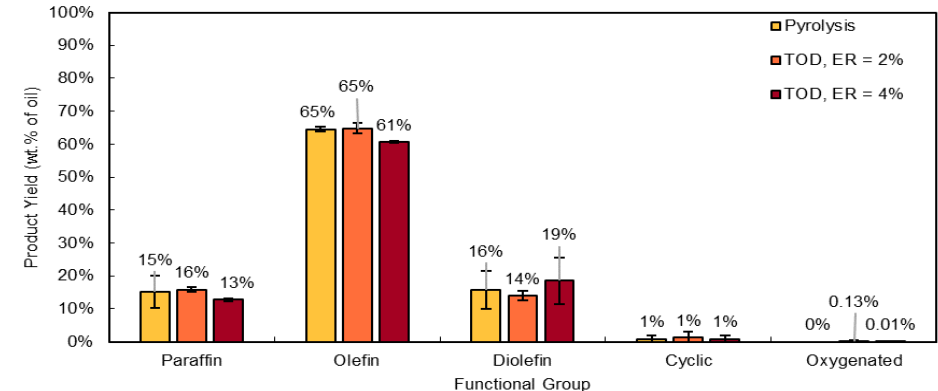
Challenges to Autothermal Operation

- Identifying thermal coupling reactions that proceed under the same reaction conditions as the driven reaction.

- Achieving close to adiabatic conditions for reactor operation.

- Assuring rapid transport of thermal energy from the products of exothermic reactions to the products of endothermic reaction.

- Applying the principle of autothermal operation to non-equilibrium processes.

- Expanding autothermal operation to low temperature processes.

Closing: A Peek at Another Impactful Although Overlooked Challenge Imposed by the Physics of Surface Area-to-Volume Ratios

The irrational expectations for batteries...

Batteries	Internal combustion engines
Power scales as surface area (watts per square centimeter).	Power scales with volume (horsepower per cubic inches, cubic centimeters or liters).
Energy capacity also scales as surface area because the solid electrolyte interphases where energy is stored in batteries are roughly fixed in thickness.	Energy capacity also scales with volume, as defined by the size of the fuel tank, not the engine itself.

Cylindrical lithium-ion battery

Top Cap (Positive Terminal)
Gasket
PTC
Vent
Cathode Tab
Top Insulator
Steel-Can (Negative Terminal)
Anode
Separator
Bottom Insulator
Anode Tab
Cathode
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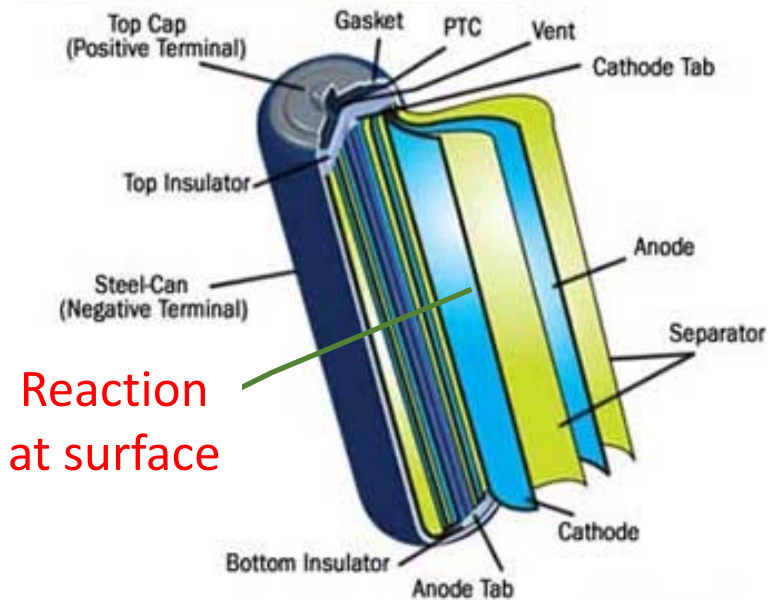
Reaction at surface
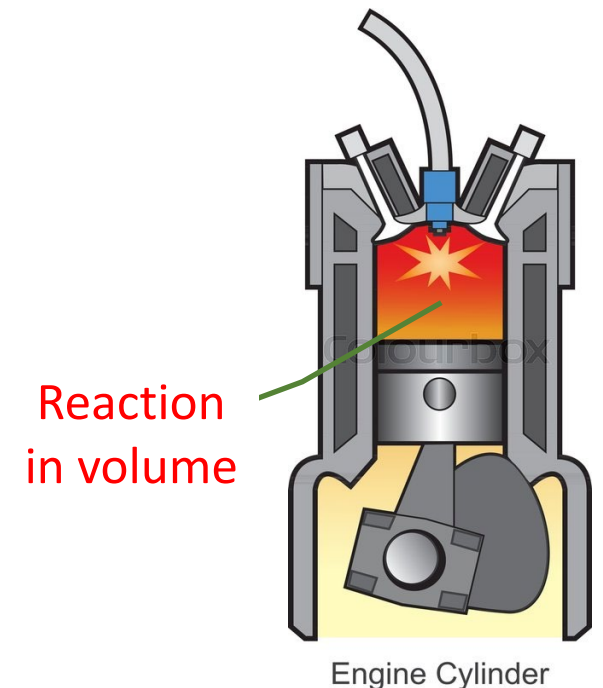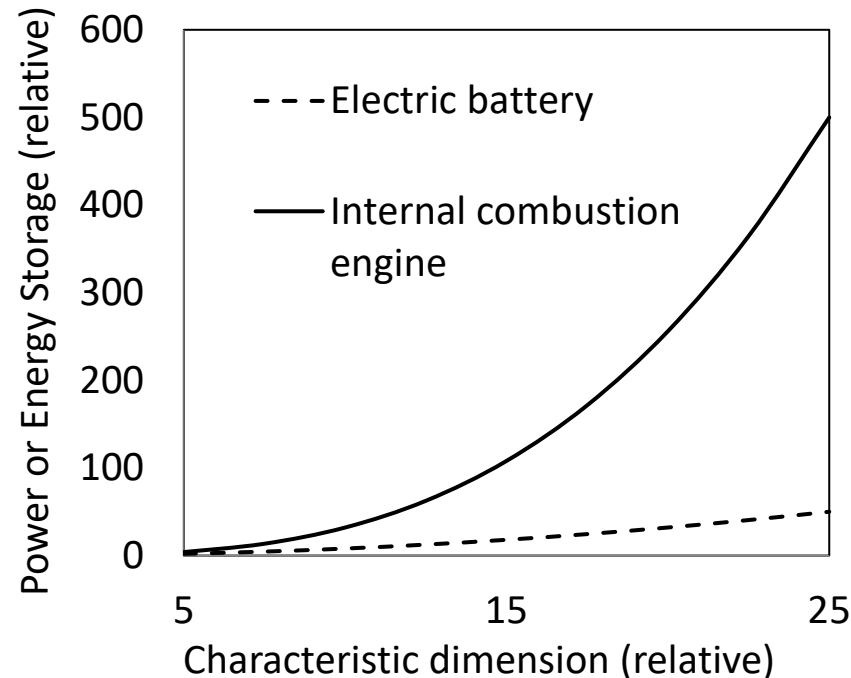
Reaction in volume

Engine Cylinder

Range anxiety isn't going away any time soon

Especially for heavy duty and long-range service

Happy to Answer Any Questions

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