

Intensification of thermochemical processes through autothermal operations

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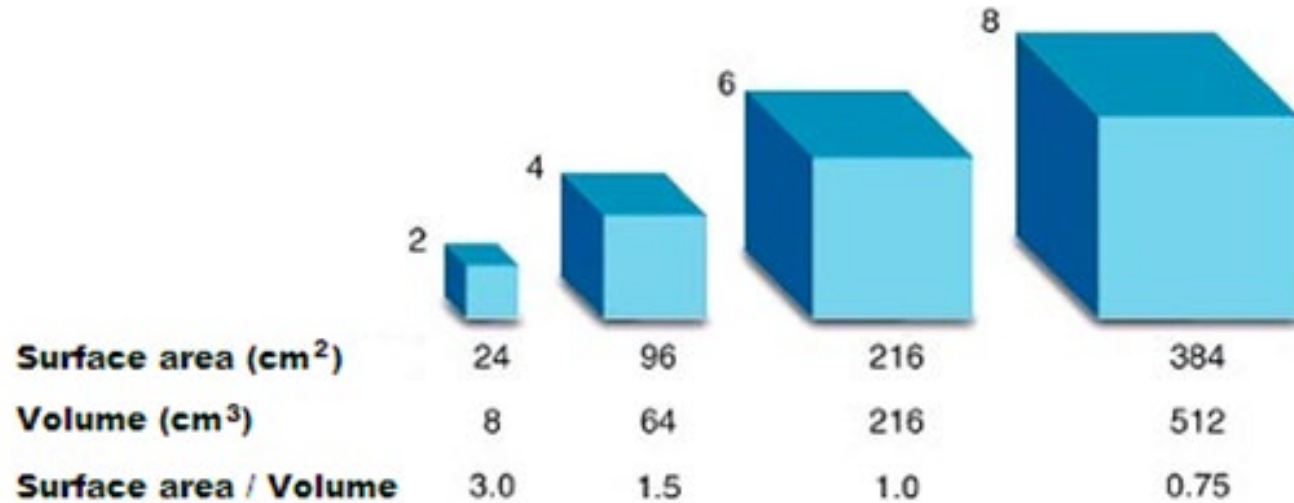
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The importance of surface area-to-volume (A/V) ratio in heat and mass transfer

Volume quickly overtakes surface area as system scales up



A mass transfer example



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 in 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

Reactor throughput for heat transfer limited vs chemical kinetically limited processes

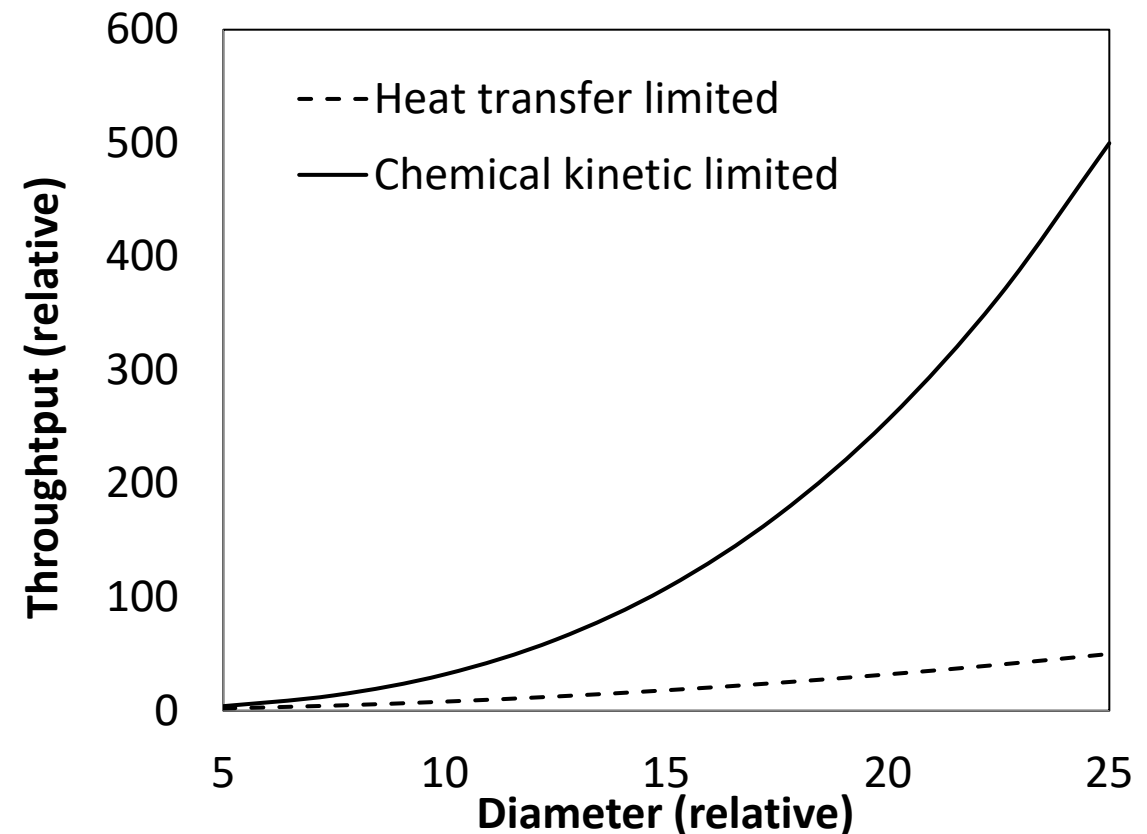
Heat transfer limited process

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

Chemical reaction limited process

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

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

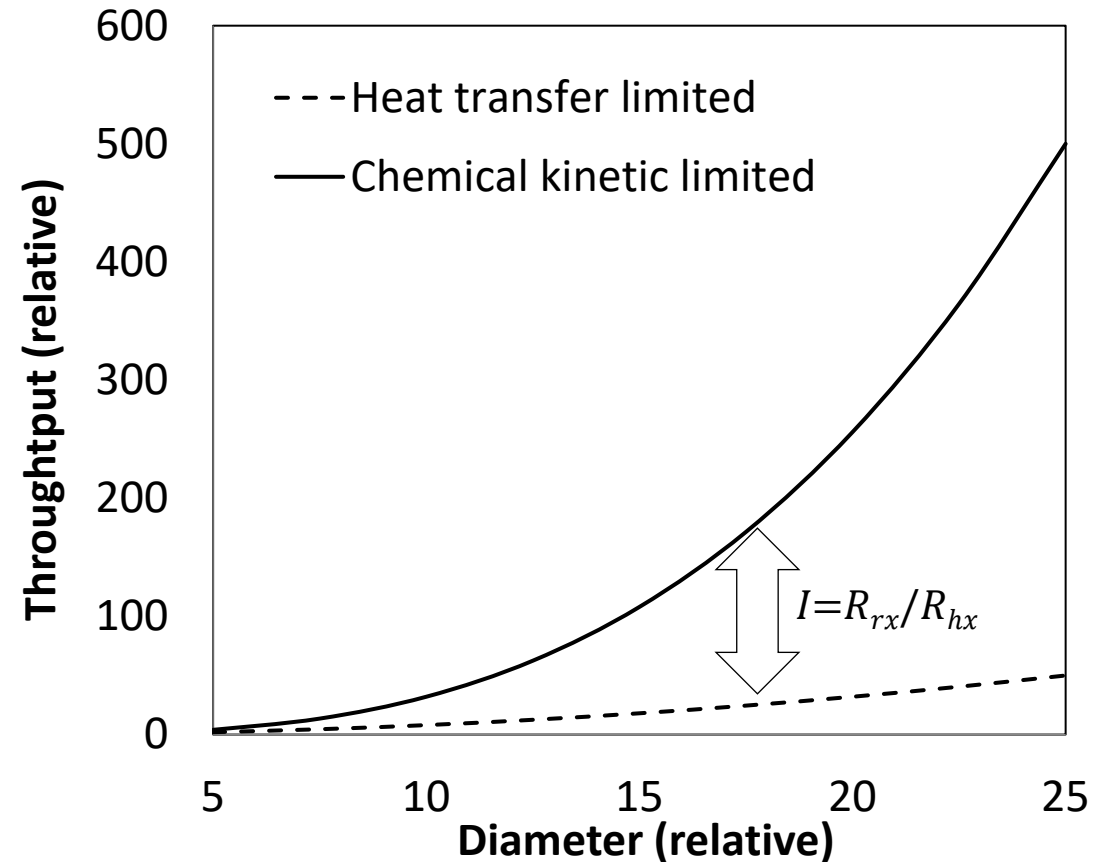


Process Intensification Scales Linearly with the Diameter of an Autothermal Reactor

Process Intensification, I

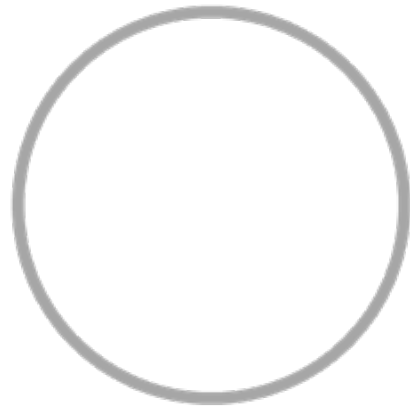
$$I = \frac{R_{rx}}{R_{hx}} = \frac{k_c C_A \varphi \left(\frac{\pi}{4}\right) D^3 |\Delta H_{rx}|}{h(T_w - T_{rx}) \varphi \pi D^2} = \frac{k_c C_A |\Delta H_{rx}|}{4h(T_w - T_{rx})} D$$

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



$$\dot{Q} \sim 2\pi DL$$

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

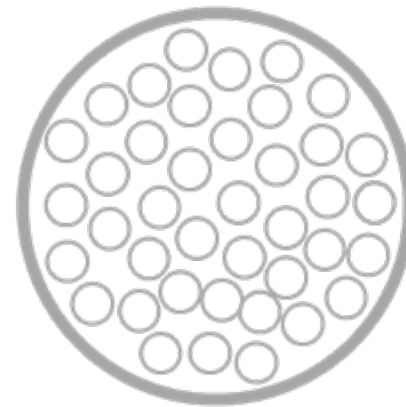
Heat transfer to/from tube array



$$\dot{Q} \sim (A_s/tube)(tubes/A_c) \pi D^2$$

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

Heat transfer to/from granular heat carrier



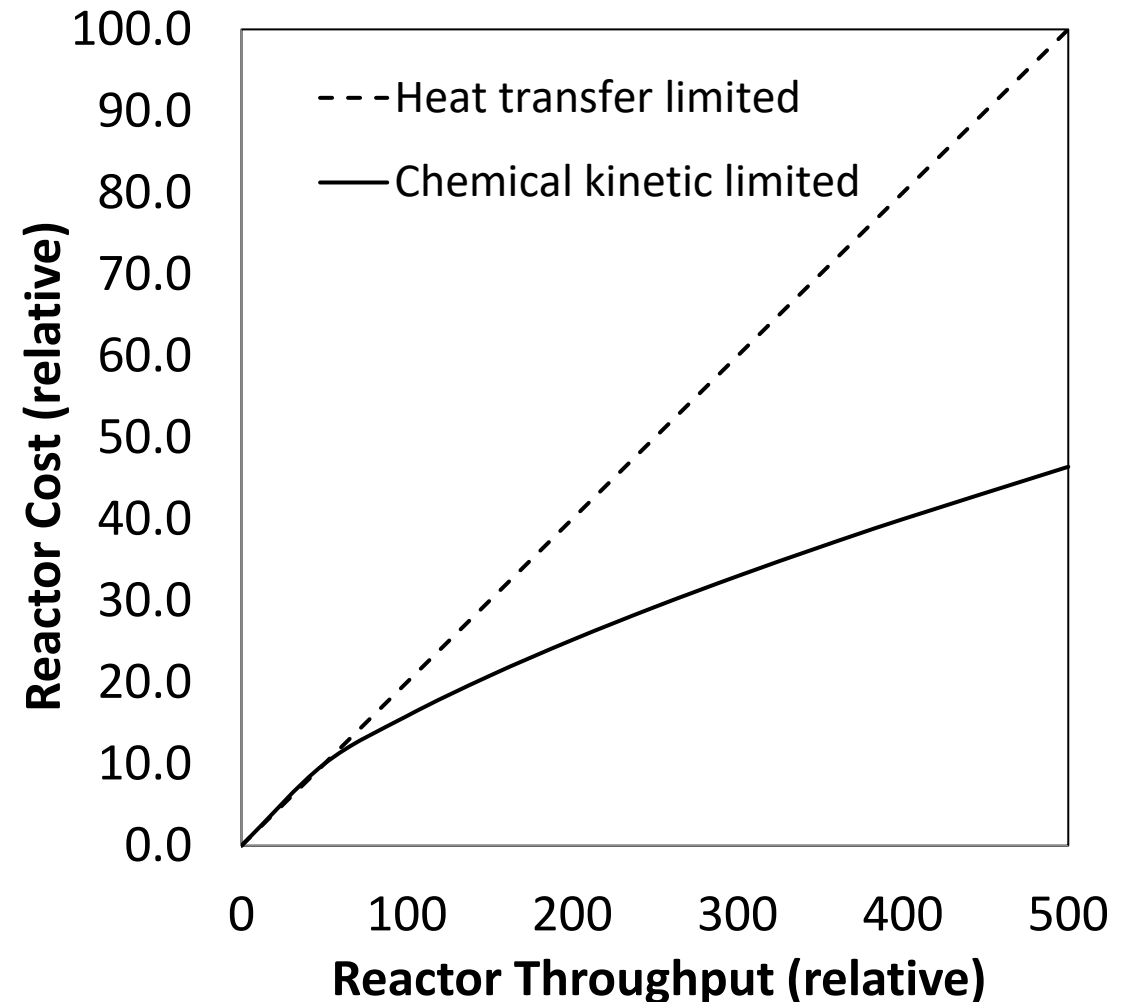
$$\dot{Q} \sim j_p (C_p \Delta T) \pi D^2$$

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

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

- Heat transfer limited process:
Since both cost and throughput scale as the square of the reactor diameter, cost of a reactor increases linearly with throughput
- Chemical kinetic limited process:
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

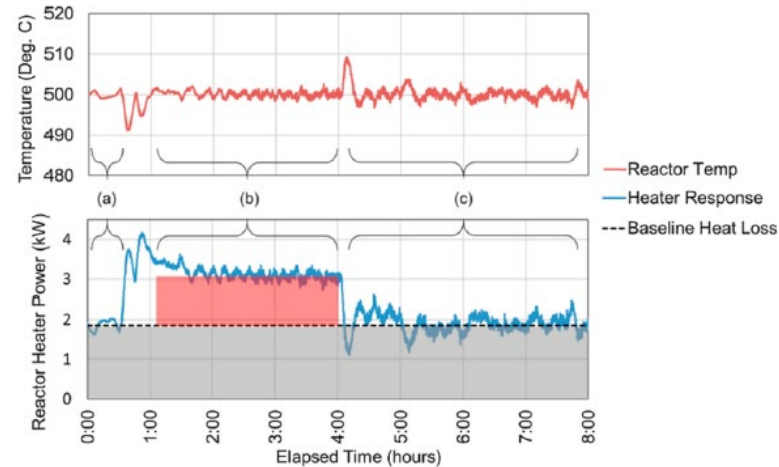
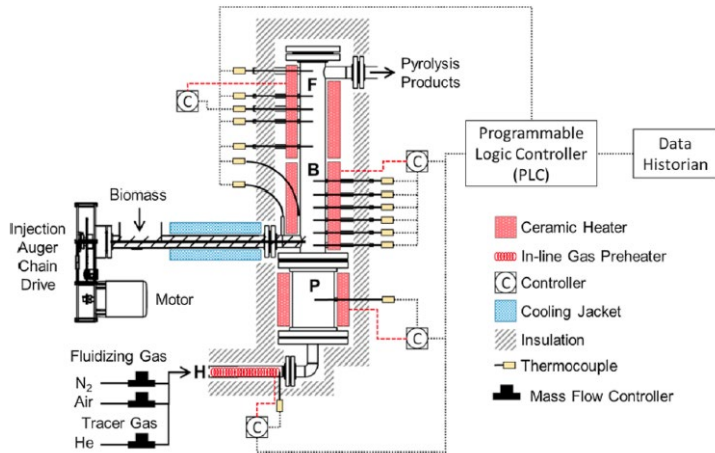
- Elimination of heat exchange simplifies reactor design
- Capital and operating costs is eliminated for ancillary equipment associated with heat exchangers including pumps, blowers, and conveyers for liquid, gaseous, and solid heat transfer media
- Dramatic increase in reactor throughput by eliminating 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)

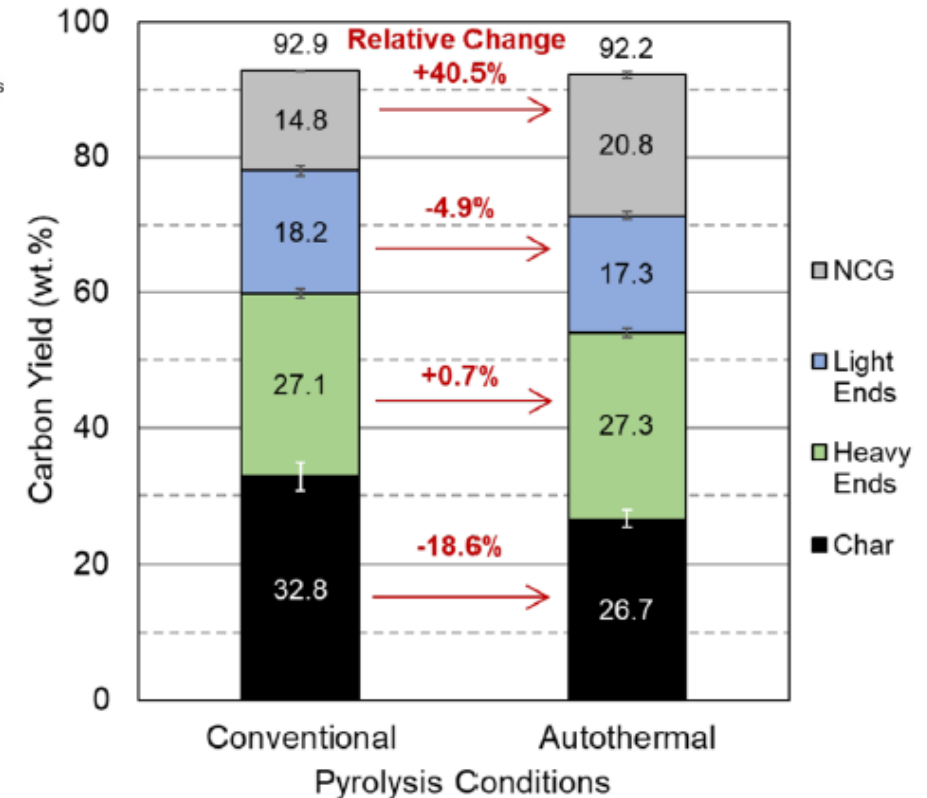
Autothermal fast pyrolysis of biomass at Iowa State University

Fluidized bed pyrolyzer assures good mixing of air and biomass



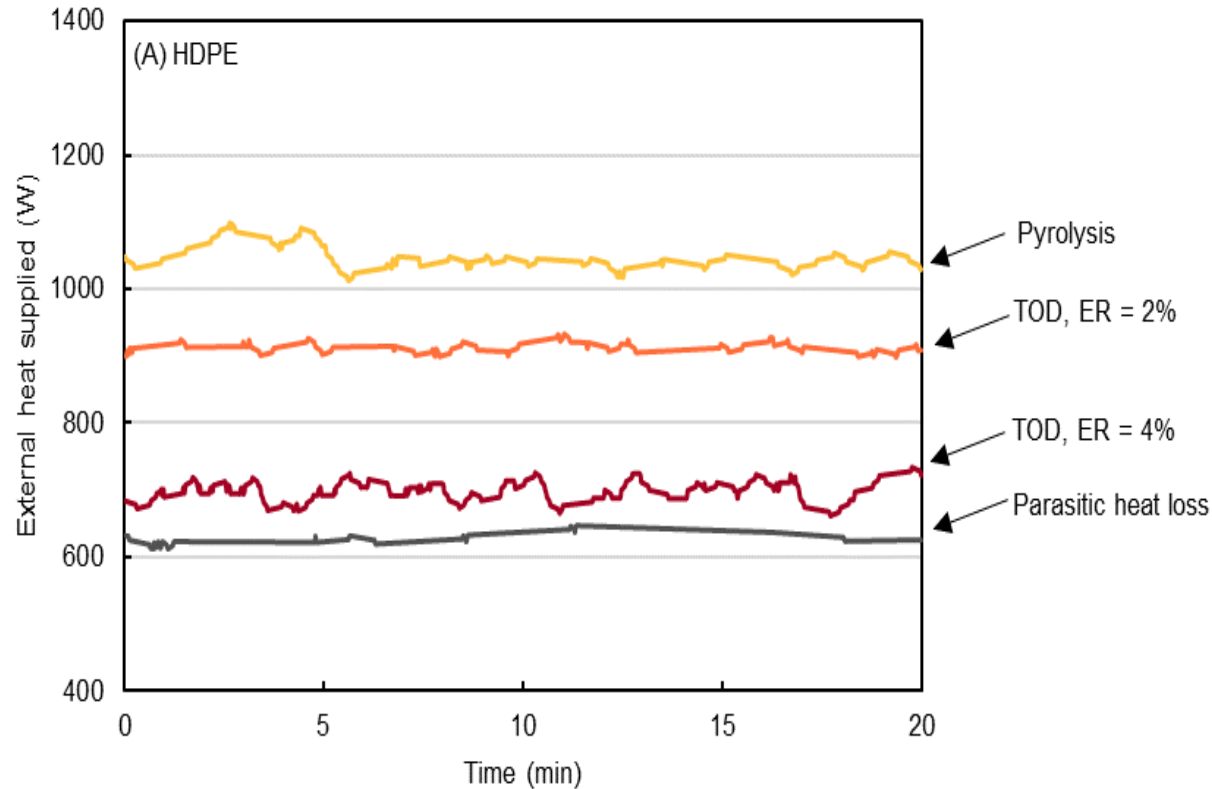
Autothermal operation achieved at 500°C for equivalence ratios as low as 0.07

Most of the enthalpy for pyrolysis comes from char oxidation

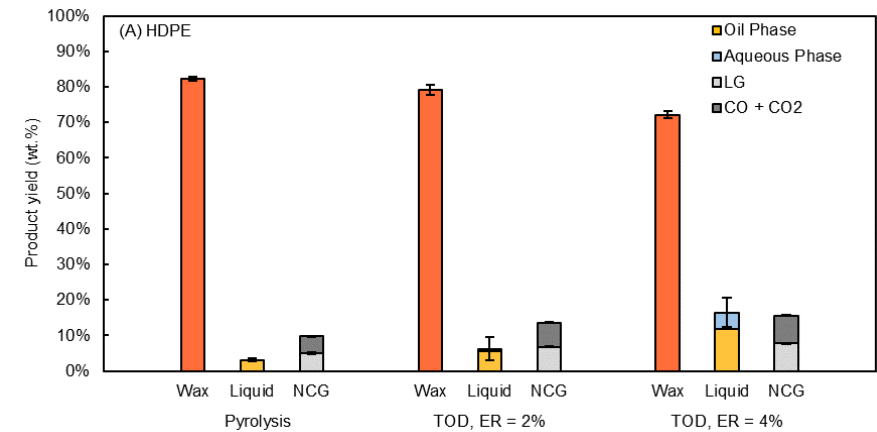


Thermal oxo-degradation (TOD) of waste plastics at Iowa State University

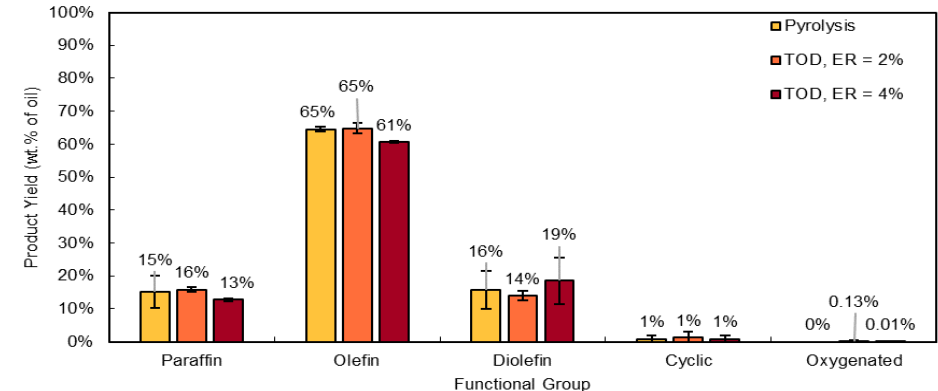
Pyrolysis of HDPE at 600°C almost autothermal at 4% equivalence ratio



Wax + liquid yield almost unchanged



Oil composition almost unchanged



Challenges to Autothermal Operation

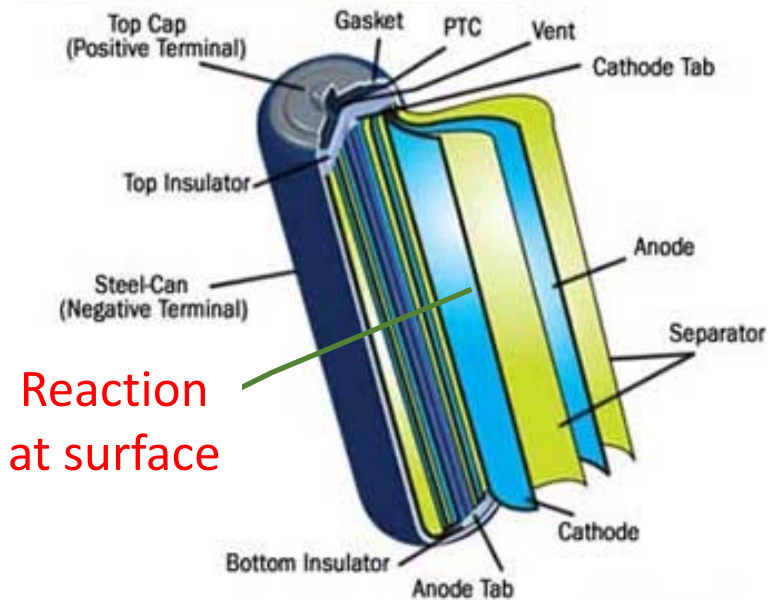
- Identifying thermal coupling reactions that proceed under the same reaction conditions as the driven reaction.
- Achieving close to adiabatic conditions for reactor operation.
- Assuring rapid transport of thermal energy from the products of exothermic reactions to the products of endothermic reaction.
- 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...

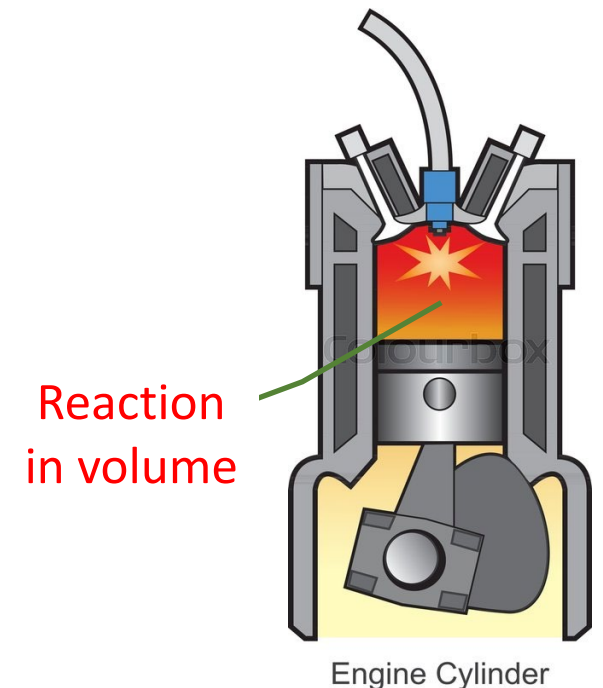
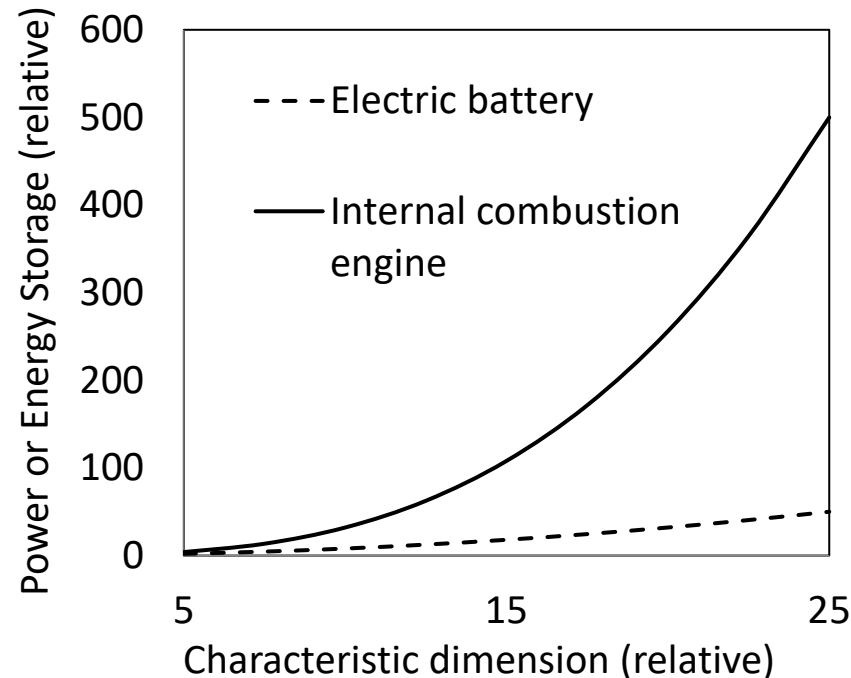
Batteries	Internal combustion engines
Power scales as surface area (watts per square centimeter).	Power scales with volume (horsepower per cubic inches, cubic centimeters or liters).
Energy capacity also scales as surface area because the solid electrolyte interphases where energy is stored in batteries 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



Reaction at surface

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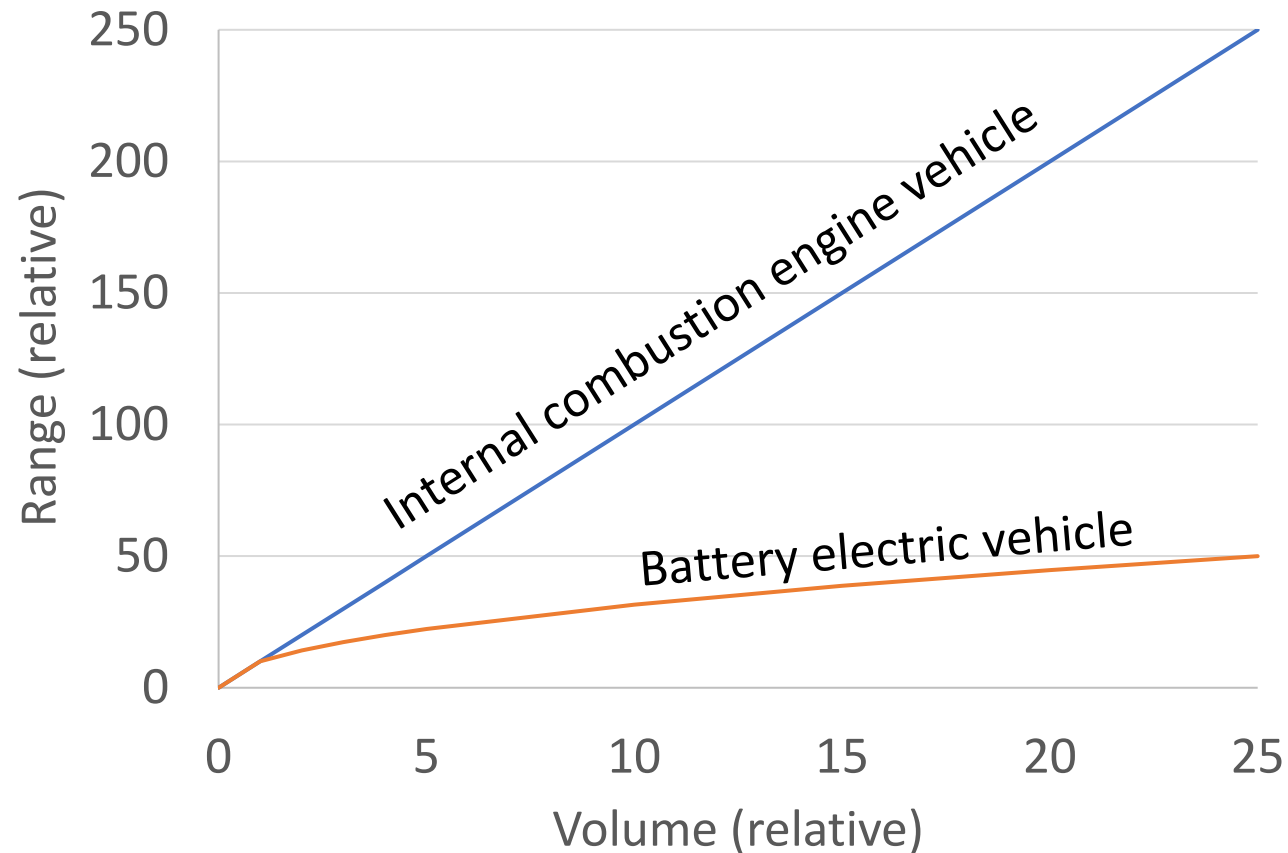


Reaction in volume

Engine Cylinder

Range anxiety isn't going away any time soon

Especially for heavy duty and long-range service



Happy to Answer Any Questions

Perspective

Process Intensification through Directly Coupled Autothermal Operation of Chemical Reactors

Robert C. Brown^{1,*}

SUMMARY

Autothermal operation of a chemical reactor involves coupling exothermic and endothermic chemical reactions for the purpose of thermal management without resorting to external energy sinks or sources. Often this is accomplished through regenerative or recuperative heat exchange between spatially or temporally separated exothermic and endothermic reactions. However, it is also possible to directly couple these reactions simultaneously within the same reactor volume, eliminating the heat-transfer bottleneck that characterizes much of chemical manufacture. It is not widely recognized that directly coupled autothermal operation allows dramatic process intensification. This perspective defines autothermal operation and contrasts it with conventional heat transfer for thermal management of chemical processes. The intensification and cost savings that can be achieved are quantified, and the implications to modular chemical process intensification are presented. Guidelines are proposed for designing directly coupled autothermal processes. Diverse examples are presented. Several challenges to expanding the field are critically discussed.

INTRODUCTION

Autothermal operation of a chemical reactor involves directly or indirectly coupling exothermic and endothermic chemical reactions for the purpose of thermal management, without resorting to external energy sinks or sources. This is often accomplished through heat exchange between spatially or temporally separated exothermic and endothermic reactions; however, it is also possible to directly couple these reactions simultaneously within the same reactor volume. In this case, heat transfer is eliminated from the process, which both simplifies the reactor design and eliminates ancillary equipment associated with providing or removing thermal energy. It also results in a dramatic process intensification, allowing much larger throughputs for a reactor of a given size than would otherwise be possible under heat-transfer limitations. As will be demonstrated, directly coupled autothermal operation is especially attractive for processes with high rates of thermal energy demand but can even benefit processes with more modest demands when heat transfer is constrained by small temperature gradients or convection coefficients.

The conventional approach to thermal management of chemical processes is heat transfer with another stream, either removing heat from an exothermic process or adding heat to an endothermic process. This management can be accomplished using either indirect heat transfer, in which the streams are physically separated by a wall through which heat is conducted,¹ or direct heat transfer, in which the two streams are physically

Context & Scale

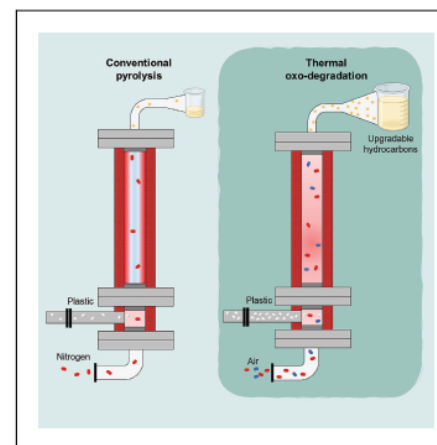
Autothermal operation combines energy-absorbing and energy-releasing chemical reactions to control the temperature of a chemical reactor instead of removing or adding heat. Eliminating heat transfer simplifies reactor design and reduces costs. Furthermore, by eliminating the processing bottleneck that heat transfer often represents, the reactor can convert reactants into products at rates much higher than are possible in a conventional reactor of the same physical dimensions. Such "process intensification" is key to advancing industries that produce energy, fuels, consumer goods, and food products. Process intensification also enables modular manufacturing in which a manufacturing plant is constructed from factory-built modules that are shipped to the construction site rather than constructed from the ground up. Instead of capturing the economic advantages of a few very large plants, modular manufacturing captures the benefits of many smaller plants close to resources and markets.



Brown, R. C. (2020) Joule 4, 2268–2289

Article

Increasing pyrolysis oil yields and decreasing energy consumption via thermal oxo-degradation of polyolefins



Thermal oxo-degradation is a form of oxidative pyrolysis used in the upgrading of plastics. Here, Brown et al. show that introduction of oxygen promotes partial oxidation of plastics, releasing heat in the reaction and decreasing external energy needs for hydrocarbon products that can be upgraded to monomers.

Jessica L. Brown, Robert C. Brown, Victor S. Cecon, Keith Vorst, Ryan G. Smith, Tannon J. Daugaard
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Highlights

Rapid plastic deconstruction using thermal oxo-degradation

Thermal oxo-degradation uses less external energy than pyrolysis

Hydrocarbon yields are preserved during thermal oxo-degradation

Brown, J. L. et al. (2024) Cell Reports Physical Science <https://doi.org/10.1016/j.xcrp.2024.101856>