

**ELECTROTHERMAL REACTOR DESIGN
AND CIRCULAR FEEDSTOCK FOR
LOW-CARBON OLEFIN PRODUCTION**

by

Arnav Mittal

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

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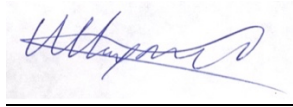
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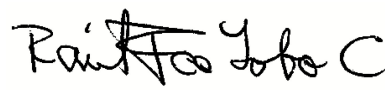
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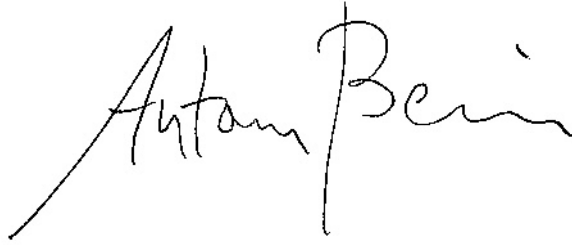
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ABSTRACT

The chemical industry is a major consumer of fossil energy and a significant source of greenhouse-gas emissions, with olefin manufacturing among its most energy- and carbon-intensive sectors. Decarbonizing olefin production requires addressing both process heat and carbon feedstocks. This thesis develops a multiscale chemical reaction engineering framework for decarbonized olefin manufacturing by integrating electrothermal reactor design with circular feedstock utilization.

First, direct electrification through Joule-heated reactors is investigated. Computational modeling is used to quantify the coupled effects of electrical conduction, heat transfer, and fluid flow in steady-state and dynamic operation, establishing how reactor design and operating conditions govern temperature control, transient behavior, and process intensification. A complementary framework for Joule-heating material and element selection is then developed to identify how material properties and structural features determine heating rate, temperature uniformity, startup efficiency, and operational stability.

These electrothermal principles are applied to short-contact-time ethane cracking for ethylene production. This work shows that internal Joule heating enables high-temperature, short-residence-time operation that increases ethylene yield while suppressing methane and aromatic byproducts relative to conventional practice. The results also indicate the potential for reduced capital costs and lower emissions when coupled with low-carbon electricity.

The thesis then addresses circular carbon integration through plastic waste valorization. Because mixed polymer melts are highly viscous, non-Newtonian, and strongly temperature dependent, transport limitations can dominate reactor performance. To overcome this challenge, a reactor-scale framework for non-isothermal multi-polymer melt processing is developed. The results demonstrate that close-clearance anchor-based configurations provide markedly better mixing, thermal uniformity, and active circulation than conventional magnetic stirring, thereby establishing practical design principles for scalable polymer processing.

Finally, we develop an integrated framework that couples microkinetic modeling and Aspen Plus process simulation for techno-economic analysis of integrated plastic-derived naphtha cracking, and Bayesian active learning to identify plastic-derived naphtha compositions that maximize the economic benefit. The results show that its economic viability depends strongly on feed composition, sourcing cost, and retrofit strategy, and that favorable integration is possible within realistic industrial constraints.

Overall, this thesis shows that decarbonized olefin manufacturing can be achieved through the coordinated design of electrothermal reactors, polymer-specific operating units, and circular feedstock integration. By linking reactor-scale transport, material selection, process intensification, and industrial deployment within a unified framework, this work provides new design principles for lower-emission and economically viable olefin production.

Chapter 1

INTRODUCTION

1.1 Decarbonizing chemical manufacturing requires redesigning both heat and carbon

The chemical industry supports modern society by supplying fuels, polymers, fertilizers, solvents, and performance materials, yet it remains one of the most energy-intensive industrial sectors and a major source of greenhouse-gas emissions.[1, 2] A large fraction of this burden arises from process heating, where fossil fuels are combusted to supply thermal energy for endothermic reactions, separations, and supporting unit operations.[3-6] Because these energy demands are embedded in large-scale continuous plants, decarbonizing chemical manufacturing is not simply a matter of replacing one energy source with another. It requires rethinking how heat is delivered, how reactors are designed, and how feedstocks move through the chemical value chain.[7, 8]

Among large-volume petrochemicals, olefins, especially ethylene and propylene, are among the most important targets for decarbonization.[9-11] These molecules are foundational building blocks for plastics, fibers, solvents, and numerous downstream intermediates.[12] Their production volumes are enormous, and their manufacture is among the most energy-intensive in the chemical industry, alongside ammonia, methanol, and benzene.[12-15] A major reason for this high energy demand is that light olefins are primarily produced by steam cracking, a process that relies on externally heated furnaces operating at high temperatures.[12] In these systems, heat

must be transferred across reactor walls into rapidly reacting hydrocarbon streams. This imposes well-known limitations: the maximum practical selectivity is constrained by tube-wall materials, heat transfer inefficiencies increase furnace duty, and temperature gradients promote secondary chemistry, byproduct formation, and coke deposition.[8, 16-20] Since olefin manufacturing sits at the core of the petrochemical industry, improving its sustainability can have a broad impact across the entire chemical supply chain.

Two complementary strategies can be used to decarbonize olefin production (Figure 1.1). The first is to replace fossil-fuel-based process heat with renewable electricity.[21-24] The second is to reduce dependence on virgin fossil carbon by introducing circular low-carbon feedstocks derived from waste plastics.[25-29] These two strategies are often discussed independently, but they are most powerful when integrated. Electrification will be transformative when reactor hardware and materials are designed to exploit it. Circular feedstocks are practical when generated at scale and integrated into existing assets without prohibitive technical or economic penalties. This thesis is built on the premise that meaningful decarbonization of olefin manufacturing requires coordinated advances in both dimensions.

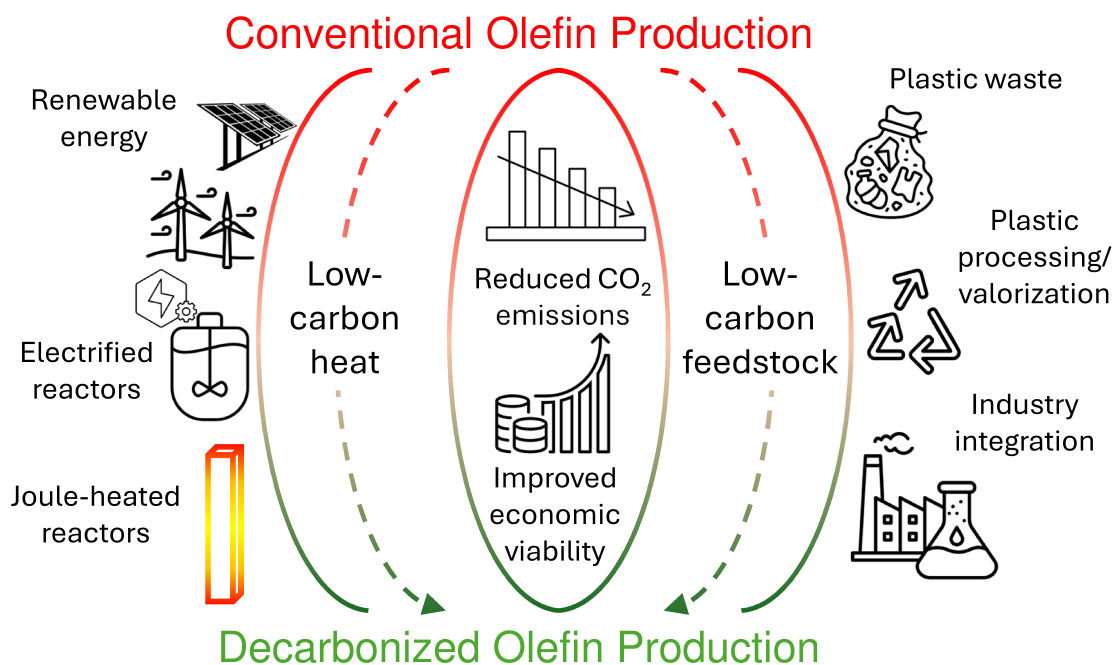


Figure 1.1: Conceptual framework for decarbonized olefin manufacturing.

1.2 Electrothermal process intensification as a pathway to low-carbon olefins

Electrothermal methods, such as microwave heating,[30-37] induction heating,[30, 38, 39] and Joule heating,[7, 8, 28, 40-43] directly convert electrical energy into heat. These technologies are particularly attractive for decarbonizing chemical manufacturing because they can be integrated with renewable electricity sources. Beyond simple energy source switching, they also offer process-level advantages, including faster heating,[28, 41, 44] lower thermal inertia, and improved controllability.[7] However, their suitability for high-temperature, continuous chemical processing varies significantly. Practical implementation depends on energy efficiency, scale-up feasibility, and the ability to sustain well-controlled thermal fields under industrially relevant conditions.

In this context, Joule heating is particularly promising (Figure 1.2). It converts electrical energy directly into heat within a resistive material, enabling localized heat generation, rapid startup and shutdown, and potentially high thermal efficiency. More importantly, it offers process-level advantages.[28, 41, 44] By generating heat internally rather than supplying it through burners or an external hot medium, Joule-heated systems can reduce heat-transfer resistance to the reacting phase, minimize temperature gradients, and access intensified operating regimes that are difficult to achieve in conventional furnace-based systems.[45] These features are especially attractive for highly endothermic, short-contact-time olefin production, where thermal control strongly influences yield, selectivity, and coking.

Joule-heated systems require a deeper understanding of reactor design, material selection, and scale-up before they can become technologically mature alternatives to conventional heating. Their performance depends on the coupled behavior of electrical conduction, heat transfer, fluid flow, and material stability. Heating rate, temperature uniformity, startup efficiency, and operational reliability are controlled by the choice of heating-element material, its geometry and porosity, and the surrounding reactor environment. For this reason, the first part of this thesis develops the electrothermal design principles needed to make Joule-heated reactors scalable and relevant to chemical manufacturing. One chapter analyzes steady-state and dynamic transport in Joule-heated reactors, while another establishes how intrinsic material properties and structural design determine electrothermal performance. These studies provide the scientific and engineering foundation for applying Joule heating to intensified olefin production.

That foundation is then applied to ethane cracking, a major route to ethylene production.[12] Conventional ethane cracking is limited by externally imposed maximum operating temperature, non-uniform heating, and the tradeoff between conversion and secondary reactions.[12] Internally heated Joule reactors create a different operating paradigm by generating heat directly within the cracking zone, enabling higher temperatures, shorter contact times, and rapid downstream quenching. In this thesis, lumped kinetics, microkinetic modeling, computational fluid dynamics, experiments, techno-economic analysis, and life-cycle assessment are combined to evaluate this intensified route. The results show that internally heated cracking can access operating windows that improve ethylene yield and suppress undesirable methane and aromatic formation relative to conventional practice.

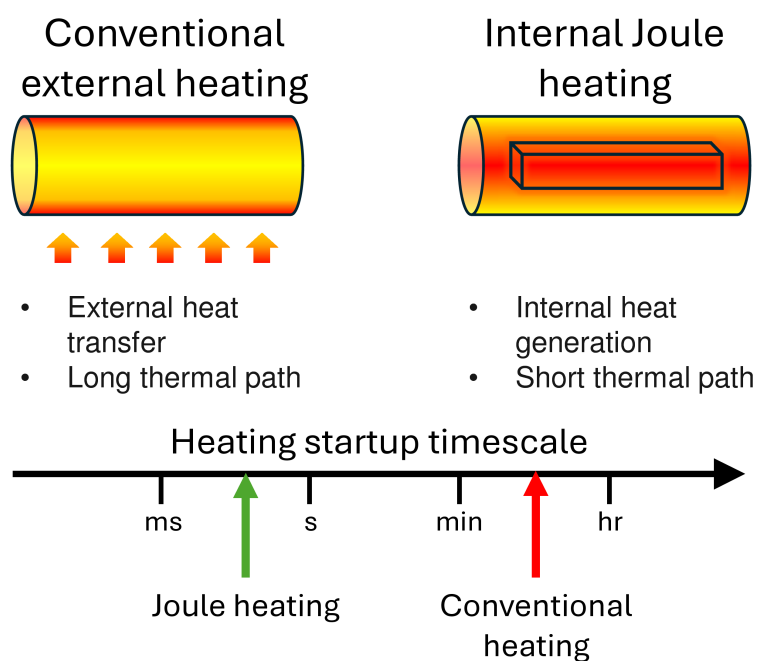


Figure 1.2: Comparison of conventional external heating and internal Joule heating.

1.3 Circular carbon requires transport-aware plastic valorization

Decarbonizing olefins through cleaner heat alone is not sufficient if the carbon entering the process remains fully fossil based.[46] This motivates the second major theme of the thesis: circular carbon integration through plastic waste valorization. Waste plastics represent both an environmental challenge and a concentrated hydrocarbon resource.[47, 48] Yet converting plastic waste into useful petrochemical intermediates is difficult because polyolefin-rich waste streams are chemically inert, compositionally heterogeneous, and often contaminated.[49, 50] While catalyst development has advanced rapidly, practical deployment depends just as strongly on the ability to process these materials under realistic reactor conditions.[49, 51, 52]

A central but often underappreciated challenge is transport in polymer melts.[53] Polyolefin melts are highly viscous, strongly temperature-dependent, non-Newtonian, and in some cases viscoelastic.[54-56] Under such conditions, mixing and heat transfer can become the dominant limitations, obscuring intrinsic catalytic behavior and complicating scale-up.[53] Laboratory stirring approaches that are acceptable in low-viscosity liquids can fail in polymer systems by generating stagnant regions, poor circulation, and large thermal gradients.[57-59] Thus, scalable plastic valorization requires not only better catalysts, but also transport-informed reactor design tailored to polymer processing.

To address this gap, this thesis develops a reactor-scale framework for mixing non-isothermal, multi-polymer melts relevant to catalytic plastic valorization. By integrating rheological measurements, constitutive modeling, computational fluid dynamics, and experiments, this work quantifies how shear thinning, viscoelasticity, temperature gradients, and impeller hydrodynamics govern reactor performance. The results show that magnetic stir bars are inadequate for highly viscous polymer melts,

whereas close-clearance anchor impellers provide substantially better mixing, thermal uniformity, and active circulation. For immiscible multi-polymer systems, coaxial impeller configurations further enhance interfacial renewal and dispersion, creating more favorable conditions for catalytic conversion. Chapter 5 provides the engineering bridge needed to turn plastic waste into processable hydrocarbon intermediates.

1.4 From plastic waste to industrial olefins: integration through plastic-derived naphtha

A key question then follows: once waste plastics are converted into hydrocarbon products, how can those products be used most effectively? Among possible targets, plastic-derived naphtha is especially attractive because naphtha is already embedded in the petrochemical value chain as a major steam-cracker feedstock.[17, 49, 51, 52, 60-63] This creates the possibility of using existing refinery and petrochemical infrastructure rather than building entirely new downstream conversion platforms. At the same time, plastic-derived naphtha is not a simple replacement for conventional naphtha. Its carbon-number distribution and hydrocarbon class composition depend strongly on upstream plastic-conversion conditions, and these differences propagate into cracked-gas selectivity, separation loads, coproduct value, and overall plant economics.[49, 51, 52]

Accordingly, the final part of this thesis examines not simply whether plastic-derived naphtha can be produced, but under what conditions it creates value in existing steam-cracking assets. To answer this, the thesis develops an integrated framework combining detailed steam-cracking microkinetics, retrofit-constrained process simulation, techno-economic analysis, and active learning. Rather than developing a completely new process flowsheet, the work preserves the essential

structure of industrial naphtha-cracking flowsheets and evaluates realistic retrofit scenarios. This reveals that viability depends simultaneously on reactor severity, retrofit configuration, feed composition, and sourcing cost. It further shows that an economically favorable plastic-derived naphtha composition need not maximize olefins alone, but should balance olefin production with coproduct value and coking tendency. In this way, the thesis links upstream plastic conversion to downstream refinery economics and moves circular olefin manufacturing closer to deployable reality (Figure 1.3).

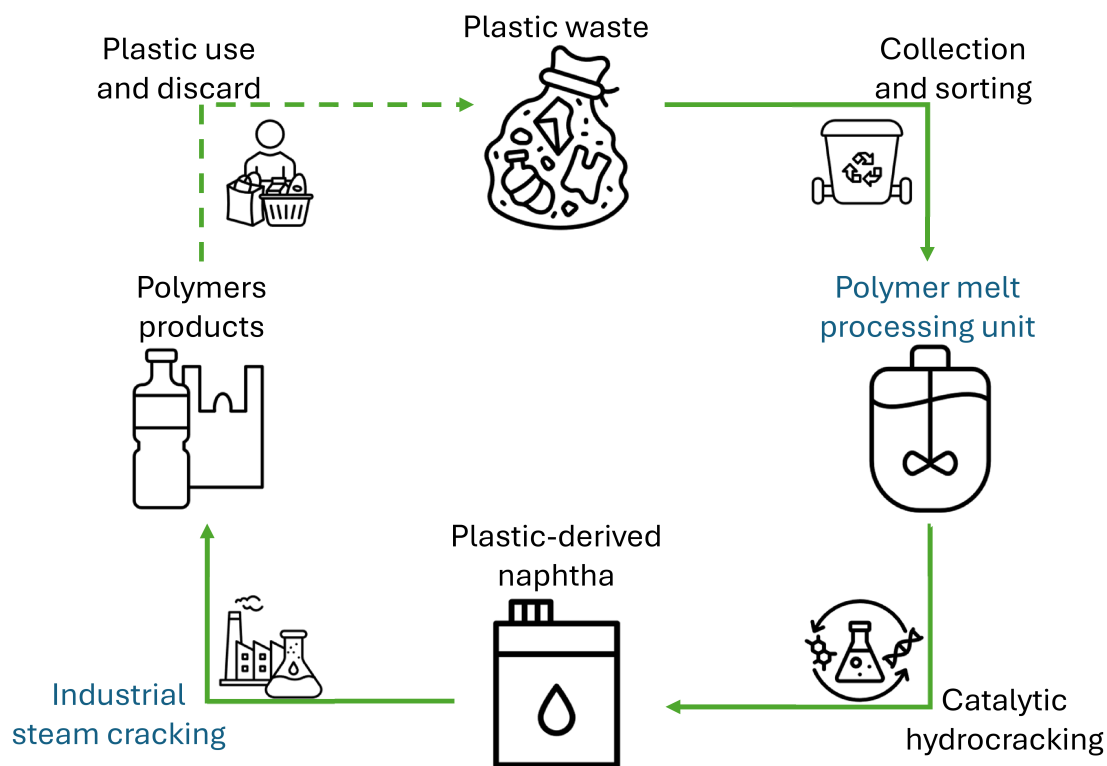


Figure 1.3: Circular-carbon pathway from plastic waste to olefin production.

1.5 Scope and organization of the thesis

Overall, this thesis presents a multiscale framework for decarbonized olefin manufacturing. At the reactor level, it establishes how Joule-heated systems can intensify high-temperature olefin production through improved heat delivery and dynamic electrothermal control. At the materials level, it identifies how heating-element properties and structure govern electrothermal performance. At the polymer-processing level, it develops the transport basis for converting waste plastics into refinery-compatible intermediates. At the process level, it determines how those circular feeds can be integrated into industrial steam cracking under realistic retrofit constraints. The central contribution is therefore not a single technology in isolation, but a strategy in which electrothermal intensification and circular feedstock integration are treated as complementary parts of the same decarbonization portfolio.

The remainder of this thesis is organized as follows. Chapter 2 examines the transport behavior of steady-state and dynamic Joule-heated reactors. Chapter 3 develops a framework for Joule-heating material and structural selection. Chapter 4 applies these electrothermal principles to short-contact-time, internally heated ethane cracking for ethylene production. Chapter 5 addresses the hydrodynamics and thermal management of highly viscous multi-polymer melts relevant to catalytic plastic valorization. Chapter 6 evaluates the retrofit integration of plastic-derived naphtha into industrial steam cracking using microkinetic, process, and economic optimization tools. Together, these chapters define a coherent pathway toward olefin manufacturing that is more energy efficient, lower in emissions, and better aligned with a circular carbon economy. Finally, Chapter 7 concludes this thesis and discusses possible future direction.

Chapter 2

COMPUTATIONAL INSIGHTS INTO STEADY-STATE AND DYNAMIC JOULE-HEATED REACTORS

2.1 Contributions

This chapter contains published work,[64] performed for the completion of this thesis. This work was performed by thesis' author.

2.2 Introduction

Manufacturing is the world's largest energy-consuming sector and the third-largest source of greenhouse gas emissions.[3-5] Process heating of chemical manufacturing accounts for 36% of the total energy consumption of the manufacturing sector.[3-6] This underscores an urgent need to develop and deploy scalable and sustainable technologies that decouple economic growth from greenhouse gas emissions to decarbonize the industrial sector using renewable electricity.[65] An effective decarbonization approach involves developing new processes for chemical production that replace fossil fuels with energy from wind and solar sources.[3] Electrification methods that convert electricity into heat, such as microwave heating,[31, 37, 66, 67] induction heating,[39] and Joule heating,[68-73] are such technologies. Among these, Joule heating is the only one that directly transforms electrical energy into thermal energy.[74]

Recent studies proposed that reactor internal Joule heating elements can eliminate heat transfer limitations from the reactor wall to the catalyst and save 2x the

energy compared to a furnace for high-temperature endothermic reactions, such as ammonia decomposition, methane reforming, high-temperature pyrolysis, alkane dehydrogenation, and plastics recycling.[33, 75] Our previous work used a carbon fiber paper (CFP) heating element and achieved very high heating rates (~ 14000 °C/s) and a near-isothermal catalyst surface.[75] Other studies[76-80] used different geometries to understand the reactor's dynamics, gas temperature contours, and the effect of reactor size on heat transfer. Despite advances, the spatiotemporal flow and temperature fields in Joule-heated reactors are hard to obtain experimentally but are crucial for efficient reactor operation.[81] Computational Fluid Dynamics (CFD) can be employed to provide temperature and flow fields non-intrusively, insights into operation, and transients with unprecedented spatiotemporal resolution.[67, 73, 82, 83]

In our study, we first compare CFD simulations with experimental data and then examine flow and temperature patterns in Joule reactors under steady state, transient, and rapid pulse heating operation. We found that carbon heating elements can achieve high, uniform temperatures, crucial for efficient catalyst use, and localize hot zones near the element to mitigate unwanted gas-phase reactions. We observed reverse flows influenced by the element's steady-state temperature. Strategies to reduce reverse flows and prevent dead zones are proposed. Heat transfer between the element and gas results in low Nusselt numbers. We also showed that rapid pulse Joule heating enhances heat transfer, essential for industrial applications. The voltage, heating element length, and the element's electrical conductivity and volumetric heat capacity enable ultra-fast heating and a short time to attain steady state. We have also developed an analytical model to describe the system's dynamics and timescales crucial for designing reactors.

This chapter is structured as follows. First, we present the computational methodology and system schematics employed in analyzing flow and temperature profiles in Joule heating reactors. This is followed by a description of the parameters for assessing the performance of the Joule heating reactor. In the results and discussion, we provide experimental validation for the CFD model, present steady-state results for a continuous Joule heated reactor and discuss transient behavior and rapid pulsing with insights from a 0D model. The conclusions highlight the key findings.

2.3 System description and computational methods

2.3.1 System description

Figure 2.1 shows the geometry of the Joule heating reactor, where V_1 represents the surface connection to the positive terminal and V_0 represents the ground connection (0 V). We model a carbon fiber paper (length (L) = 38 mm, width (L_w) = 8 mm, and thickness (L_{th}) = 0.21 mm, refer to Table 2.1 for material properties) contained within a quartz tube (radius (r) = 11 mm, length (L_t) = 80 mm) in continuous gas flow. A constant voltage V is applied across the carbon fiber paper.

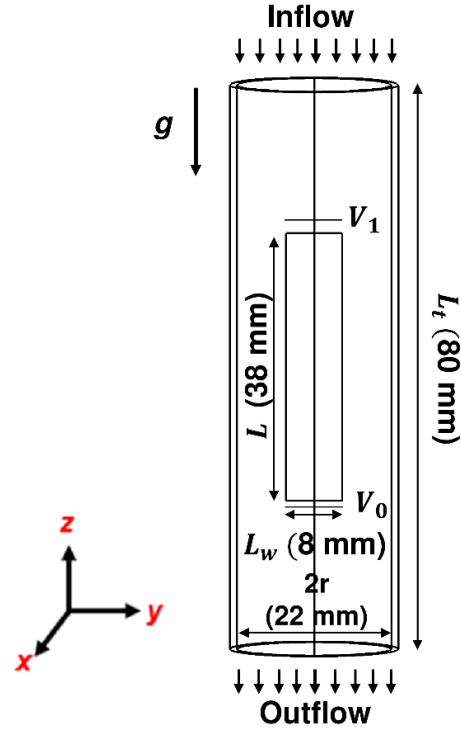


Figure 2.1: Schematic of the Joule-heated reactor modeled in COMSOL.

2.3.2 Models and computational methods

We solve the electric current, fluid dynamics, and heat-transfer equations. The current density J in the carbon fiber paper is described using the Maxwell-Ampere law[84, 85]

$$J = \sigma E + \frac{\partial D}{\partial t} + J_e \quad (2.1)$$

where σ is the electrical conductivity, E is the electrical field intensity, D is the electric displacement, and J_e represents the externally generated current. Eq. 2.1 is combined with Eqs. 2.2 and 2.3.

$$E = -\nabla V \quad (2.2)$$

$$\nabla \cdot J = 0 \quad (2.3)$$

Eq. 2.2 defines the electric field, and Eq. 2.3 imposes charge conservation.[84, 85]

The power density dissipated into a medium, denoted as P_e , is described as[84, 85]

$$P_e = \frac{\partial(\frac{1}{2} \varepsilon_0 \varepsilon_r E \cdot E)}{\partial t} \quad (2.4)$$

where ε_0 is the permittivity of vacuum and ε_r is the relative permittivity of the material. Eq. 2.4 can be rewritten as $\sigma E \cdot E$. Combining this with Eq. 2.2 results in inverse of the resistance times the square of voltage difference applied ($\frac{V^2}{R}$). The dissipated power serves as a heat generation term in the energy balance equation (Eq. 2.5).[84]

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p U \nabla T = -\nabla(\kappa \nabla T) + P_e \quad (2.5)$$

Here, T denotes the temperature, ρ is the mass density, C_p is the specific heat, U is the velocity, and κ is the thermal conductivity. To evaluate the spatial temperature field and the temperature field inside the Joule heating element, the energy balance equation is solved together with Eqs. 2.1 - 2.3, the continuity equation for compressible fluids (Eq. 2.6), and the Navier-Stokes equation (Eq. 2.7).[84]

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho U) = 0 \quad (2.6)$$

$$\frac{\partial(\rho U)}{\partial t} + \nabla \cdot (\rho U \times U) = \mu \nabla^2 U - \nabla P + \rho g \quad (2.7)$$

In Eq. 2.7, μ is the dynamic viscosity and P denotes the pressure. The aforementioned governing equations are implemented and solved using the COMSOL Multiphysics software,[86] referenced hereafter as COMSOL. The AC/DC module, the heat transfer

module, and the laminar flow module are employed for time-dependent, three-dimensional simulations and solved using inbuilt finite element solvers. A 2D axisymmetric model is not used due to the non-axisymmetric nature of the heating tape and 3D non-symmetric vortex formation.

Figure 2.2 illustrates the boundary conditions of the model. All Joule heating element surfaces except the terminals are electrically insulated. At the carbon paper-gas interface, the tangential component of the electric field and the normal component of electric displacement are considered continuous. Heat loss due to natural convection is imposed outside the quartz tube. We also consider radiation loss from all surfaces of the carbon fiber paper to the environment. The initial temperature is 20 °C. The temperature at the inlet (T_g^{in}) is 20 °C, and a zero gradient boundary condition is applied at the outlet. A zero gradient for pressure and no-slip boundary condition for velocity are imposed at the tube wall. A zero gradient and constant velocity are used for the pressure and velocity at the inlet, respectively. At the outlet, the velocity has zero gradient, the backflow is suppressed, and the pressure is constant (atmospheric). A mesh dependency was performed to ensure discretization-independent results (Figure A.1). We have utilized a fine general physics mesh for the heating tape and normal for the quartz tube and the fluid dynamics. The emissivity and effective voltage faced by the element were adjusted by matching the predicted temperature and current to our previous experiments (see also below and Table 2.1).[75]

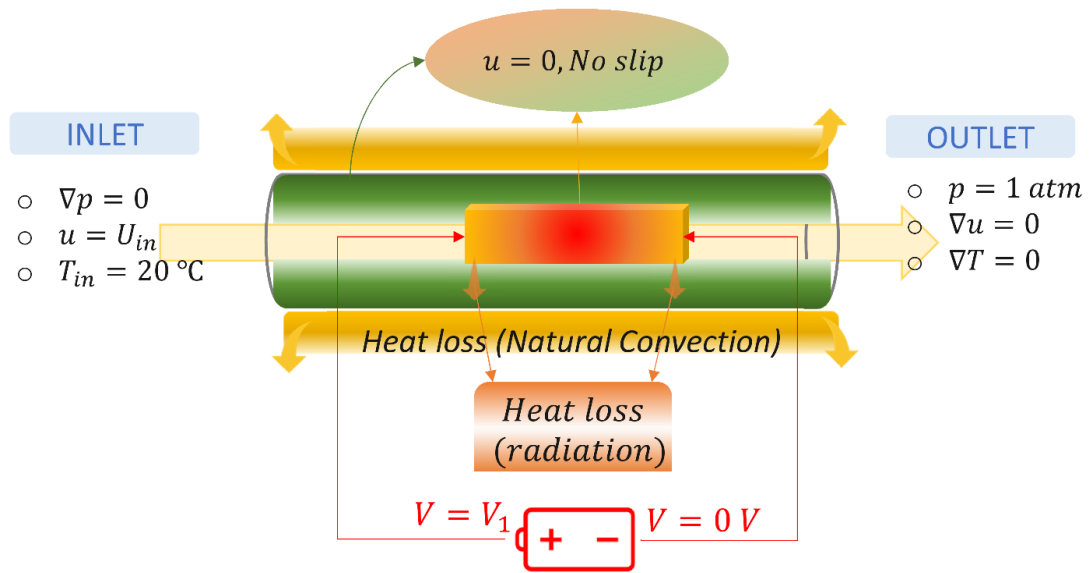


Figure 2.2: Schematic of boundary conditions used in the Joule-heated reactor model.

Table 2.1: Carbon fiber paper properties. T is the temperature in Kelvin.

Material Property	Carbon Fiber Paper Values
Thermal conductivity [W/(m*K)][87, 88]	400
Density [kg/m ³][89]	452.38
Heat capacity [J/(kg*K)][90]	2253+0.038*T-3.8 105/T
Electrical conductivity [S/m][75]	1/[0.00021*[0.76-0.000113*(T-273.15)]]
Relative permittivity [1][91]	4960
Emissivity (this work with data from Ref[75])	0.68
Effective voltage (this work with data from Ref[75])	0.97* V

Flow dynamics is primarily influenced by interfacial, viscous, and gravitational (buoyant) forces. To understand the relevant forces, we compared nitrogen (N_2) and helium (He) as a carrier gas (see Table 2.2 for gas properties calculated at 20°C using the in-built COMSOL material module). These gases share similar volumetric heat capacity (density x heat capacity) but the density, mass-based specific heat, thermal conductivity, and viscosity differ substantially. To assess the presence of reverse flow, we use the criterion of *Visser et al.*[92, 93] Reverse flow exists when the axial component of the velocity (u_z) falls below -0.1 times the average axial velocity (u_{avg}). In dimensionless form, reverse flows are prevented when the ratio of the Grashof number (Gr) to the Reynolds number (Re) (Eq. A.1 and Eq. A.2),[92, 94] is smaller than α_{crit} . α_{crit} can be determined by increasing the inlet flow rate for given conditions until no reverse flow occurs.

Table 2.2: Properties of gases at 20 °C. Temperature dependence is included in COMSOL.

Property (20 °C)[86]	Helium (He)	Nitrogen (N ₂)
Density (kg/m ³)	0.16	1.16
Viscosity (Pa*s)	1.95 x 10 ⁻⁵	3.805 x 10 ⁻⁵
Thermal conductivity (W/(m*K))	0.15	0.06
Heat capacity (J/(kg*K))	5195	1040
Volumetric heat capacity (J/(m ³ *K))	852.0	1206.4

To investigate the axial variation of heat transfer from the element to the gas, we calculated the Nusselt number (Nu, Eq. 2.8) along the heating element in the wide dimension (x-direction in the ZX plane, refer to Figure 2.1) using Eq. 2.9.[93-95]

$$Nu = \frac{hD}{\kappa} \quad (2.8)$$

$$Nu = \frac{dT_g}{dx} * \left(\frac{D/2}{T_w - T_\infty} \right) \quad (2.9)$$

In Eq. 2.8, h is the heat transfer coefficient and D stands for the diameter of the reactor. In Eq. 2.9, T_w is the temperature just adjacent to the element, and T_∞ is the gas temperature far away from the element. The temperature gradient normal to the element ($\frac{dT_g}{dx}$) was evaluated using a 3 point forward finite difference scheme with a step size of 0.105 mm by metanalysis of the CFD data.

To support insights regarding flow and heat transfer, we estimated the carbon tape heating and cooling rates (upon turning the power off), the time to reach steady state, and the steady state temperature (refer to Figure A.2 for details). $\overline{T_{e,ss}}$ is the carbon tape spatial average steady state temperature. Steady state is achieved when $\frac{\overline{T_e(t)} - \overline{T_e(t-\Delta t)}}{\overline{T_e(t-\Delta t)}} < 0.001$, where $\overline{T_e}$ is the temperature spatial average over the volume of the heating element and Δt is the time step. t_{ss} corresponds to the time elapsed to

reach the steady state temperature. The heating rate is the slope of the fit from the initial temperature to $0.9 \cdot \overline{T_{e,ss}}$. The cooling rate is determined similarly when the temperature decreases upon turning the power off.

The temperature uniformity of the element at steady state is evaluated using the coefficient of variation (CV).[96] CFD also solves the heat equation inside the heating element. As both faces of the element are symmetric, the temperature profile for one of the surfaces (T_s) is used to calculate the CV.

$$CV (\%) = \frac{Std(T_s)}{\overline{T_s}} \times 100 \% \quad (2.10)$$

A high CV means a non-uniform element temperature; conversely, a low CV indicates a uniform element surface temperature.

To gain insights, a simple 0D model for an isothermal element is also derived below. The validity of the assumption is discussed in the Results and Discussion section. The element's temperature, T_e , evolution is described using a simple energy balance across the element volume:

$$\frac{d(\rho C_p V_s T_e)}{dt} = Q_{eh} - Q_{cond} - Q_{rad} \quad (2.11)$$

$$Q_{eh} = \sigma \left(\frac{V}{L} \right)^2 V_s \quad (2.12)$$

$$Q_{cond} = hA(T_e - T_a) \quad (2.13)$$

$$Q_{rad} = e \Sigma A(T_e^4 - T_a^4) \quad (2.14)$$

where all physical properties pertain to the solid material, V_s is the solid volume (length (L) times width (L_w) times thickness (L_{th})), Q_{eh} is the electrical heating rate,

Q_{cond} is the heat rate lost to the flowing gas, Q_{rad} is the radiative heat loss rate, h is the heat transfer coefficient between the solid and gas, T_a is the ambient temperature, e is the emissivity, Σ is the Stephan-Boltzmann constant, and A is the (total) exposed surface area.[22, 23]After combining Eqs. 2.11 – 2.14, we solve the model using the odeint library in Python.

2.4 Results and discussion

2.4.1 Comparison to experimental data

Experiments from previous work[75] was used to validate our CFD model. The experiments consist of a vertical tubular reactor made of quartz with gas flowing from top to bottom. The CFP element is held by two stainless steel clamps and four copper plates, and a DC power supply provides the current for Joule heating. We compared our predictions with the CFP element's steady state temperature under continuous operation at various voltages with *He* flowing at 90 mL/min using the infrared (IR) camera (Optris PI 1M or PI640). CFD temperatures for continuous Joule-heated reactors at various voltages are in excellent agreement with experimental data (Figure 2.3a), with a relative deviation of <0.5%. The insets show an IR camera image highlighting the experimental element temperature uniformity. Experiments shows that the heating element remains stable experimentally over days of operation. Longer time on stream data will be valuable. Under adiabatic conditions, one would expect high wall temperatures and materials stability would need attention.

Figure 2.3b compares our prediction with the element surface temperatures for transient operation with the voltage turned on and then off for three settings. The IR camera had a lower detection limit (the solid lines are truncated at long times).

Additional validation data is shown in Table A.1. Given that the properties of the materials are not as accurately known, especially their temperature dependence, the model predictions are satisfactory.

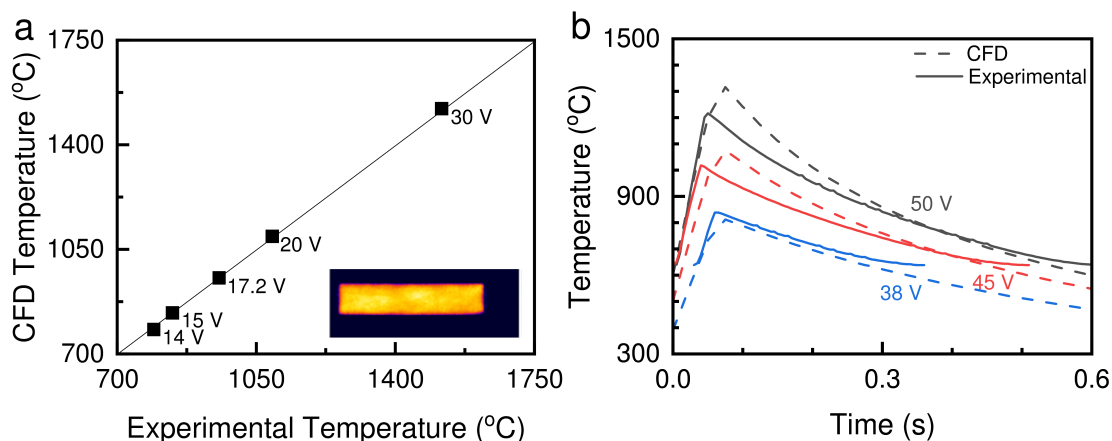


Figure 2.3: Comparison of CFD and published experimental data¹⁸. (a) Average steady-state element's surface temperature for continuous Joule-heated reactors at various voltages with He, flowing at 90 mL/min (element's length = 38 mm, width = 8 mm, and thickness = 0.21 mm). The inset shows IR data indicating the temperature uniformity. (b) Transient data for rapid pulse Joule-heated reactors (50 ms of heating and 950 ms of cooling). The IR camera detects down to 638.5 °C and thus, cooling-phase transient data below this temperature is not shown).

2.4.2 Steady-state flow and temperature in continuous Joule-heated reactors

The majority of the literature Joule-heated reactors operate at steady state (a continuous Joule-heated reactor).[23, 42] Thus, we first investigate the Joule heated reactor's temperature followed by flow at steady state.

Highly endothermic reactions, such as propane dehydrogenation or methane reforming, need high temperatures, which can also trigger undesired gas phase reactions. Joule heated reactors using a CFP element can provide high temperatures

while minimizing undesirable reactions.[75, 76] For example, how localized the temperature field is near the heating element is unclear. We analyze the temperature field without reactions to provide insights. Figure 2.4a-d shows isotherm contours on two planes (ZX and ZY) parallel to the z-axis at various *He* flow rates. The gas temperature remains high only near the heating element. It decreases with increasing distance (x and y-axis distance) from the heating element. Lower inlet gas flow rates (Figure 2.4a-c) result in the incoming gas being heated near the entrance of the reactor, due to heat transfer upstream, whereas higher inlet flow rates (Figure 2.4d) result in heating of the gas after a certain distance from the entrance. Figure 2.4e depicts the temperature contours for the element, showing negligible change with increasing inlet flow rate. The temperature of > 80% of the surface is within 15 K (1805 K – 1790 K). The edges, especially near the entrance, are slightly colder (~1770 K) than the center (~1805 K). Overall, the temperature gradient along the surface is small (< 2% of the maximum temperature and the coefficient of variance (CV) < 0.1%), i.e., the surface is almost isothermal despite the very high temperature. Unlike temperature gradients in other Joule-heated reactors, e.g., external wall-heated, the carbon heating tape leads to very efficient and uniform catalyst utilization.[75]

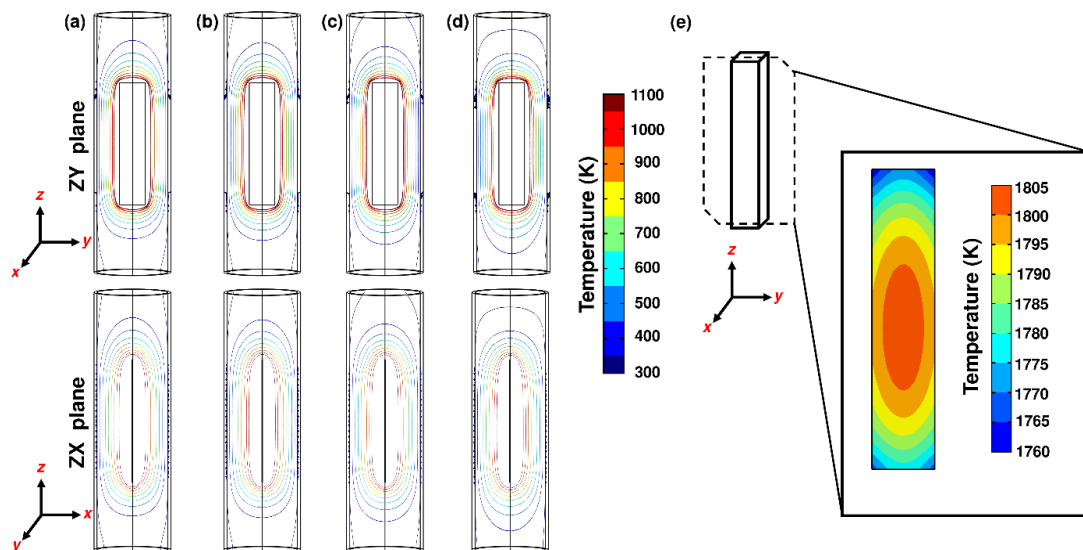


Figure 2.4: Temperature isotherms at steady state for 30 V applied for a He inlet flow rate of (a) 90 mL/min, (b) 180 mL/min, (c) 360 mL/min, and (d) 720 mL/min. (e) Temperature contours of the element surface (ZY plane) at steady state for 30 V applied.

The radial distance between isotherms in the gas is constant, implying a roughly constant spatial temperature gradient. The gas temperature profile between the element and the quartz tube remains similar when changing the inlet flow rate, and the reactor has fixed hot and cold regions at steady state. High temperatures happen on the catalyst and a hot zone contained only near the element; the gases experience rapid cooling away from the heating element (at ~ 5 mm axially and ~ 8 mm radially, the temperature has dropped from 1700 K to 600 K). This localized hot zone confined to the element, as seen in Figure 2.4, aligns with prior hypothesis that the gas remains cold. The CPF behaves unlike *Wismann et al.*[79] FeCrAl element, who found significant temperature gradients across it due to its lower thermal conductivity. This rapid cooling significantly reduces the likelihood of undesirable gas phase side

reactions. The rapid quenching of the gas phase and reduced coking by gas chemistry, consistent with experiments,[76] is a novel characteristic of the heating tape.

As the gas inlet flow rate increases, the gas heat-carrying capacity increases, shifting the isotherms downwards (along the + z-axis). The z-distance between the isotherms upstream of the element decreases. Conversely, the z-distance between contours downstream of the element increases, i.e., as the inlet flow rate increases, the distance required for cooling downstream becomes greater. The gas cools and heats faster with increasing inlet flow rate.

Here we assess the effect of increasing inlet gas flow rate on both the outlet gas temperature ($\overline{T_{g,ss}^{exit}}$) and element's average temperature ($\overline{T_{e,ss}}$) (Figure 2.5a) for the two gases. The tape temperature is very high despite the relatively low voltage applied and the heat losses (discussed next). Clearly, one can achieve catalyst temperatures unachievable by conventional means. Surprisingly, despite the high heating element temperature, the exit gas temperature is hardly above room temperature. As the inlet flow rate increases, $\overline{T_{g,ss}^{exit}}$ increases gradually for *He* and $\overline{T_{e,ss}}$ increases slightly. This aligns with the increase in the gas expansion observed with increasing inlet flow rate. For *N₂*, $\overline{T_{e,ss}}$ is higher by approximately 100 °C and $\overline{T_{g,ss}^{exit}}$ is slightly comparable to *He*. $\overline{T_{g,ss}^{exit}}$ increases with an increase in the inlet gas flow rate as the gas removes more energy from the element.

We analyze the energy dissipation to understand the low outlet temperature despite the element's high temperatures. Most of the power supplied is lost through radiation (Figure 2.5b). A small fraction is lost through conduction from the element surface to the gas, which is then convected and conducted toward the quartz tube. This energy is eventually carried away by the air circulating outside the quartz tube. The

quartz tube power loss through radiation is negligible, due to its low temperature ($\sim 20^\circ\text{C}$). The remainder of the power supplied is carried by the outlet gas (this is a very small fraction). Owing to the low thermal conductivity of N_2 , the power transferred to the quartz tub is reduced. This results in diminished power loss to the environment as compared to He (6% vs. 21.8%), consistent with the results in Figure 2.5a. The data highlights a potential strategy for enhancing power efficiency by minimizing radiative power loss through radiation reflection (Figure A.3 shows the element's temperature profile when we trap radiation). At these high heating elements temperatures, radiation dominates heat losses, as expected, the heat transfer to the gas is slow, and the heat losses from such a microsystem are huge that the exit gas is hardly warm.

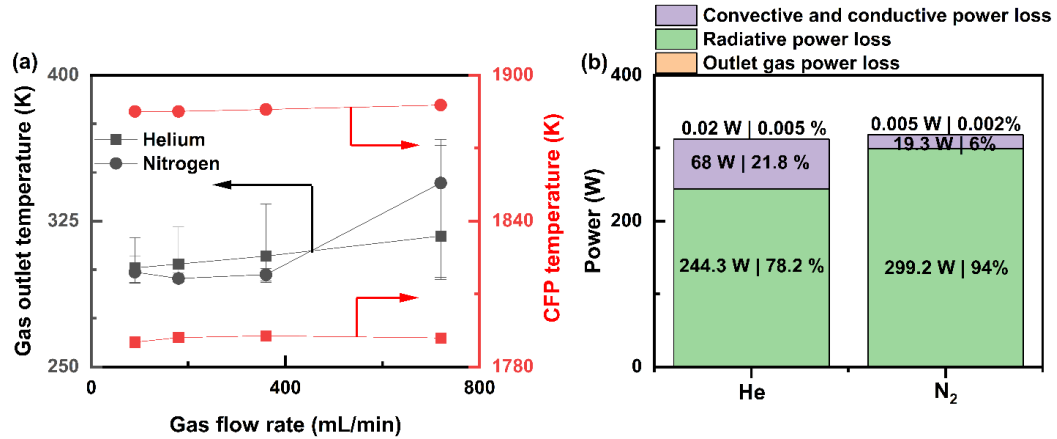


Figure 2.5: Steady state temperature and power distribution. (a) Average element and average gas outlet temperatures at steady state vs. gas flow rate. Conditions: 30 V (Error bars represent the maximum and minimum gas outlet temperature). (b) Power distribution when a power of ~ 312 W is applied to CFP, at steady state, using N_2 or He, each with an inlet flow rate of 90 mL/min.

A similar analysis was conducted for $\overline{T_{e,ss}} \sim 1000$ °C and 600 °C, with N₂ flowing, as shown in Figure A.4. At 1000 °C (methane reforming temperatures), radiation remains the primary power loss mechanism, accounting for about 70% of the total, but is now comparable in magnitude to the conduction power loss. At 600 °C (propane and ethane dehydrogenation temperature), radiation and conductive power losses are comparable. The reduction in the radiation power loss (and the corresponding increase in the conduction power loss) as $\overline{T_{e,ss}}$ decreases is attributed to the T^4 dependency of the radiation term. This highlights the significance of employing an adiabatic system. At these temperatures, $\overline{T_{e,ss}}$ changes negligibly (< 1%) with increasing gas flow rate.

The temperature profile of the gas influences the velocity profile (and vice versa). This interplay between temperature and velocity results in different flow patterns that can either improve or hinder reactor performance. In Joule heated reactors, we observe reverse flow facilitated by buoyant forces due to the cool gas entering the reactor and contacting the hot element, inducing a density difference. These buoyant forces are countered by the inertial and viscous forces. This is illustrated in Figure 2.6 which shows the axial velocity on the ZY plane at various inlet flow rates. Positive velocity means an upward gas flow; negative implies downward motion. Figure 2.6a–c indicates reverse flow. As inertial and viscous forces become strong, no reverse flow is seen at higher inlet flow rates, e.g., 720 mL/min (Figure 2.6d).

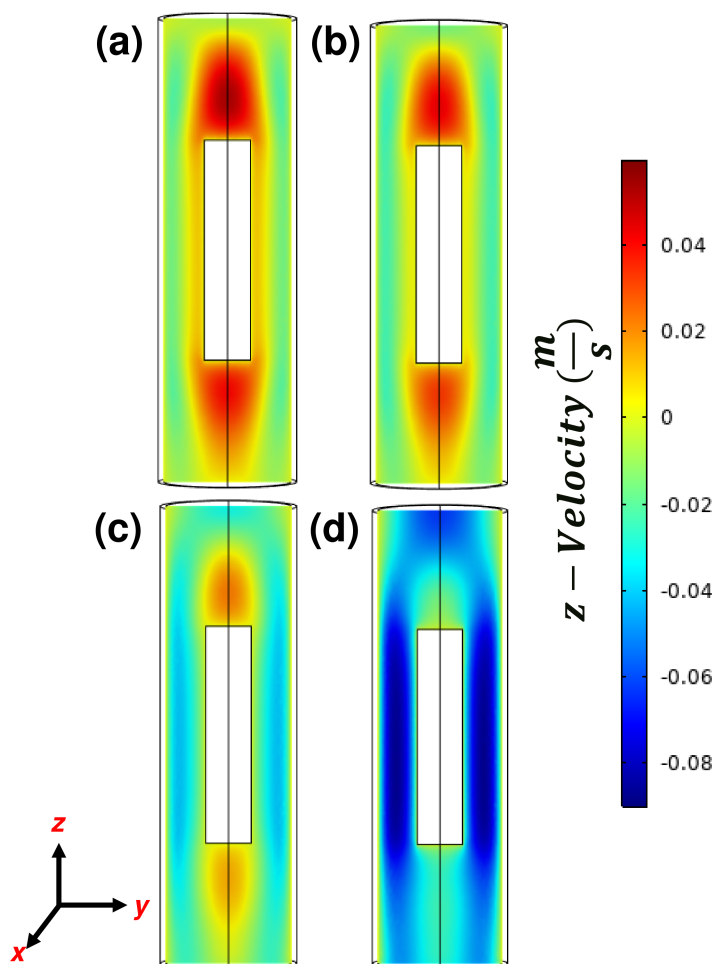


Figure 2.6: Axial velocity on the ZY plane of the heating element with 30 V applied and He inlet flow rate of (a) 90 mL/min, (b) 180 mL/min, (c) 360 mL/min, and (d) 720 mL/min.

Reverse flow affects the vertical velocity (z-component), altering the flow's overall magnitude and direction. Figure 2.6 illustrates the velocity magnitude on the plane perpendicular to the heating element (XZ plane) at various inlet flow rates. Figure A.5 shows the velocity magnitude in ZY plane. Low inlet flow rates result in reverse flows, with the maximum velocity magnitude seen above the element.

Comparatively, a lower velocity magnitude occurs below the element (Figure 2.7a). A minimum velocity magnitude occurs near the walls. As inertial and viscous forces increase with increasing inlet flow rate, the velocity magnitude builds up around the element and decreases above and below the element. Hence at high flow rates (Figure 2.7d), a significantly higher velocity is seen around the element, whereas a minimum is seen above the element and near walls. Figure 2.7a-c also shows vortices above and below the element because of the reverse flow. Despite minimal reverse flow in Figure 2.7c, most of the gas flows near the walls avoiding the reverse flow near the element. A forward flow is seen in Figure 2.7d.

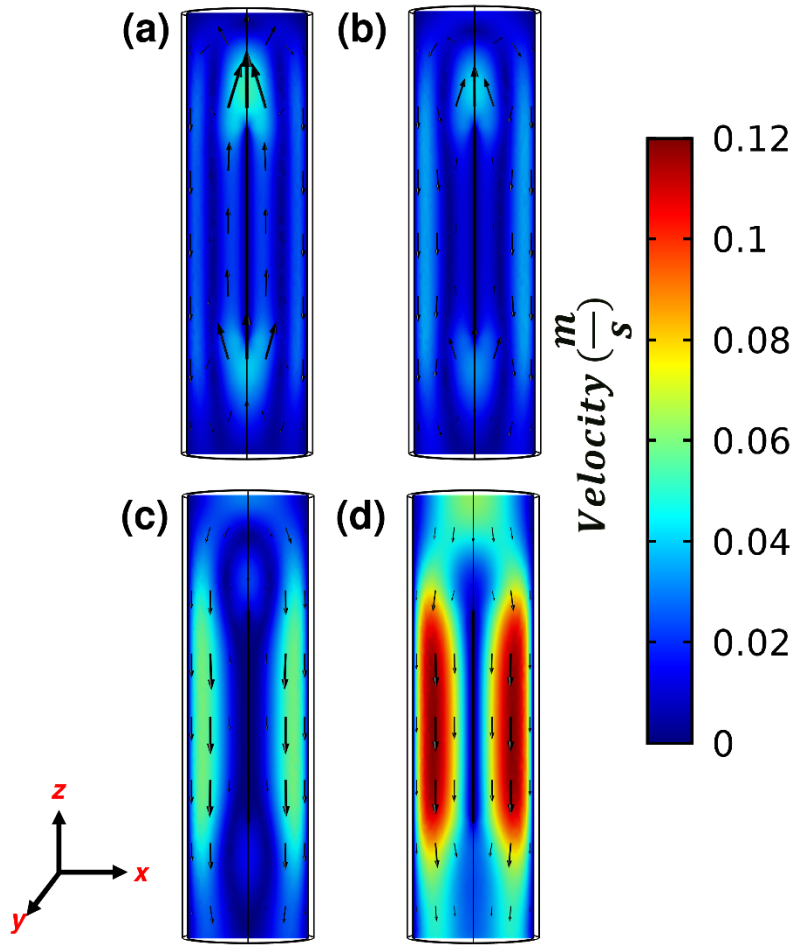


Figure 2.7: Velocity magnitude and direction of flow on the plane perpendicular (ZX plane) to the heating element with 30 V applied and He inlet flow rate of (a) 90 mL/min, (b) 180 mL/min, (c) 360 mL/min, and (d) 720 mL/min.

We compare the axial location of maximum velocity magnitude for various flow rates in Figure 2.7. Figure 2.7 presents the maximum velocity magnitude within the XY plane (refer to Figure 2.1), perpendicular to the reactor axis, versus position at steady state. The expected maximum velocity profile in the XY plane typically shows an increase from the inlet up to the element, followed by a region where the velocity remains constant over the element, and then a decrease toward the outlet. This pattern

is attributed to the flow dividing into two distinct streams when it encounters the element. Figure 2.8 reveals this expected trend only when the inlet flow rate exceeds 360 mL/min, i.e., under minimal reverse flow. For lower inlet flow rates, there is a peak in velocity before reaching the heating element (vortices formation), followed by a region of nearly constant velocity over the element. Remarkably, at low inlet flow rates, such as 90 mL/min, a secondary peak in velocity appears after the element.

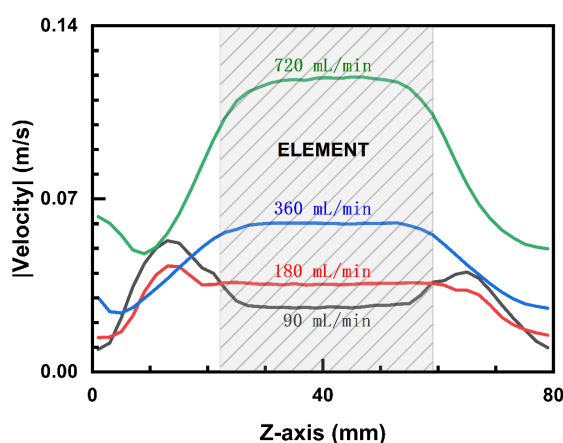


Figure 2.8: Maximum velocity magnitude vs. axial position from reactor top to bottom. Shaded region represents the space parallel to the element. 30 V was applied for various He flow rates.

Reverse flows have been observed when high-temperature elements interact with gas flows, such as horizontal and vertical metal-organic chemical vapor deposition (MOCVD) reactors. It has been found that reverse flow significantly affects the reactor temperature uniformity.[97, 98] In MOCVD reactors, a cold gas finger at specific velocities was seen and attributed to reverse flows, a phenomenon also influenced by gas properties. For instance, a stable flow was observed above 80

cm/sec for *He* and hydrogen (*H₂*) while *N₂* and argon (*Ar*) consistently exhibit unstable flows.[98] Reverse flow leads to instability in laminar flow profile, causing entrance effects.[99, 100] Furthermore, they create dead zones and minimize yield in chemical reactors.[92, 94] In MOCVD reactors, the heating element is typically placed near the reactor wall, and transient operations have not been studied.

As mentioned above, the onset of reverse flow is often characterized by α_{crit} , which depends on the heating rate (Figure A.6 shows α_{crit} for various heating rates) due to its effect on the thermal boundary layer, indirectly influencing the buoyant force and the amount of gas traveling backwards. We regressed α_{crit} at various voltages for He, yielding Eq. 2.15, where R_h stands for the heating rate and α_{crit} is the critical value at a given heating rate.

$$\alpha_{crit} = 8.145 * R_h + 14206 \quad (2.15)$$

This equation was assessed using *N₂* (refer to Figure A.7 for the axial flow velocity profile of *N₂*). Consistent with Eq. 2.15, increasing the fluid's flow rate and kinetic viscosity suppresses recirculation, whereas increasing the tube radius promotes recirculation. Similarly, due to its low kinetic viscosity, *N₂* promotes reverse flow. High flow rates are necessary to avoid flow recirculation, consistent with literature findings in MOCVD reactors.[98] Similarly, due to low thermal conductivity of methane and propane, significant reverse flows may occur in continuous Joule-heated reactors. *Zhang et al.*[78] reported that an incompressible fluid tends to underestimate the temperature at lower flow rates and overestimate it at higher flow rates. This would be due to enhanced heat transfer due to recirculation at lower flow rates. The overestimation could result from gas expansion lowering the residence time over the heating element. Operating under α_{crit} leads to reverse flow, allowing the gas to pass

through the heating element (hot region) multiple times and enhancing heat transfer. However, this can create dead zones with unreacted mass, thus reducing the overall reactor efficiency. These zones may also cause flow irregularities, as depicted in Figure 2.7. In smaller reactors, it would lead to significant entrance length effects. Therefore, it is essential to optimize the inlet flow rate to minimize dead zones while maintaining some energy recirculation.

Figure 2.9 shows the variation of the Nu number along the length of the heating element for varying inlet flow rate. We observe an asymmetric U-shaped profile for all inlet flow rates, with high Nu values ~ 4.5 at the start and ~ 3.8 near the end of the element, possibly due to vortex formation leading to faster heating of the gas than the middle of the element. A constant value of ~ 1.4 is observed over most of the element. Interestingly, the inlet flow rate has no obvious effect on the Nu number. This occurs when the heat transfer between the element and the gas is dominated by free convection, manifested with a high Richardson number ($Ri = \frac{Gr}{Re^2} = 843 \gg 1$ in our system, $Gr \sim 2$ and $Re \sim 0.06$). [101, 102] This also means that the thermal boundary layer is governed by the buoyant force and gas expansion (variables such as gas properties and $\overline{T_{e,ss}}$) rather than the inertial or viscous forces. A constant Nu reflects a fully developed laminar flow and a low Gr number. [101]

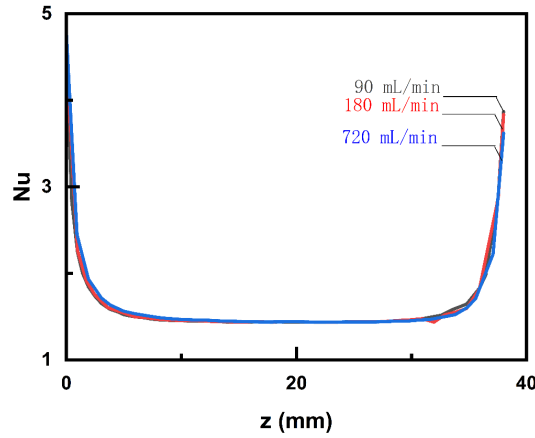


Figure 2.9: Impact of inlet flow rate on the Nu number vs. distance from the leading edge of the heating element at steady state. 30 V applied to CFP.

A similar analysis for an incompressible flow gave an average $Nu \sim 2$ (results shown in Figure A.8). This implies that compressibility has some effect on heat transfer.[94] When $Ri \gg 1$, the empirical correlation (Eq. 2.16) for a hot vertical plate can be used[102] for a Rayleigh number $Ra \leq 10^8$

$$Nu_L = 0.68 + \frac{0.663 * Ra^{0.25}}{\left(1 + \left(\frac{0.492}{Pr}\right)^{\frac{9}{16}}\right)^{\frac{4}{9}}} \quad (2.16)$$

In Eq. 2.16, Pr is the Prandtl number (see Eq. A.3 and Eq. A.4, for definitions). Eq. 2.12 predicts the Nu_D ($Nu_D = Nu_L * \frac{D}{L}$) is 1.23 compared to 1.4 shown in Figure 2.9.

2.4.3 Dynamic Joule heating

Time scales play a crucial role in the design of continuous and pulsed Joule-heated reactors. Each CFD simulation takes 6-12 h computing time using 36 CPU's

(Intel E5-2695 V4) on a high-performance computing cluster to obtain a solution of a given pulse. Here, we exploit an analytical, dynamic, spatially homogeneous (0D) model for rapidly predicting the temperature of the Joule heating element, the time to reach steady state, and the heating and cooling rates. The model is grounded on the isothermicity of the element due to its high thermal conductivity. The heating time scale for the gas is Section A.3. In evaluating the results of CFD and this simple model, one should keep in mind the element material's physical constraints, e.g., the melting temperature, and use realistic physical parameters.

Our model predicts the heating rate (R_h), the temperature at steady state ($T_{e,ss}$), and the time to reach steady state (t_{ss}) within 15% of the CFD data (refer to Figure A.9 for parity plots). We can get further insights by introducing the dimensionless temperature, the catalyst residence time based on the inlet velocity (U_{in}), and the associated dimensionless time.

$$\theta = \frac{T_e}{T_a} \quad (2.17)$$

$$t_0 = \frac{L}{U_{in}} \quad (2.18)$$

$$\tau = \frac{t}{t_0} \quad (2.19)$$

Eq. 2.11 becomes

$$\frac{d\theta}{d\tau} = \alpha - \beta * (\theta - 1) - \gamma * (\theta^4 - 1) \quad (2.20)$$

$$\alpha = \frac{\sigma \left(\frac{V}{L}\right)^2 * t_0}{\rho C_p T_a} \quad (2.21)$$

$$\beta = \frac{Nu}{Pe} * \left(\frac{r^2}{L * L_{th}} \right) * \left(\frac{\rho_g C_{p,g}}{\rho C_p} \right) \quad (2.22)$$

$$\gamma = \frac{e \Sigma A T_a^3 t_0}{\rho C_p V_s} = \frac{t_0}{Bo} \quad (2.23)$$

α, β , and γ are dimensionless constants, Pe is the heat transfer Peclet number ($Pe = t_{cond}/t_{conv} = \frac{\frac{r^2}{\kappa}}{\frac{L}{U_{in}}} = \frac{r^2 * U_{in} \rho_g C_{p,g}}{L * \kappa}$, where t_{cond} is the heat conduction time scale, t_{conv} is the heat convection time scale, and r is the radius of the tube), and Bo is the Boltzmann number ($Bo = \frac{\rho C_p V_s}{e \Sigma A T_a^3}$, with the dimension of time, in s).[103]

α, β , and γ represent the dimensionless rate of Joule heating and losses due to gas conduction/convection and radiation, respectively. α includes the key physical properties of the element (electrical conductivity and volumetric heat capacity), its geometric length, and the voltage. The strongest dependence of α is on the voltage, V^2 . As one changes variables while keeping a constant residence time, the dependence on the heating element length L is also strong, L^{-2} . Without such a constrain, the dependence of α on physical properties and length is linear or inverse linear. One can increase the Joule heating rate by increasing the voltage, selecting a heating element material with high electric conductivity and low volumetric heat capacity, and a short length.

β includes the ratio of the thermal conduction rate to the thermal convection rate (Pe), the ratio of convective to conductive heat transfer across the boundary of the element and the fluid (Nu), the ratio of the tube's radius squared to geometric features

of the heating element, $r^2/(L * L_{th})$, and the ratio of the gas' volumetric heat capacity to that of the element. Increasing the heat transfer coefficient (h) or the element's length leads to increased heat loss to the gas (β). Increasing the element's volumetric heat capacity and element's thickness (L_{th}) leads to a decreased heat loss to the gas. Increasing the element's emissivity (e) and decreasing the element's thickness (L_{th}) or volumetric heat capacity (ρC_p) leads to increased γ (radiative losses). These dimensionless constants exhibit distinct order of magnitude, with $\alpha \sim 10 - 10^2$, $\beta \sim 10^{-3}$ for gases and ~ 10 for liquids, and $\gamma \sim 10^{-2}$. For this work, the geometric factor is $r^2/(L * L_{th}) \sim 15$. Since $\theta > 1$, the last term in Eq. (2.20) can attain values of $\sim 10^1$ at high temperatures. The dominance of α in Eq. 2.20 highlights the importance of the element's material selection and design (length).

Eq. 2.20 can be simplified for endothermic reactions essential for production of chemicals into four temperature ranges, as shown in Table 2.3. We utilized the 0D model to estimate the maximum power required by the CFP to achieve the desired temperature range, using the maximum temperature as the input to the model. The table provides an estimate of the steady state temperature, the heating time scale (t_H) that is the characteristic time scale for the response of the system, and implicitly the time to steady state ($5t_H$) assuming constant material properties.

Table 2.3: Temperature ranges for producing essential chemicals, examples of reactions, power required, and equations for estimating the steady state heating element temperature and heating time. The power depends on the length, thickness, and gas utilized, considered here as 38 mm, 0.21 mm, and He respectively.

Range	Temperature Range (°C)	θ Value	Power Required by CFP (W)	Examples of Reactions	Heating element temperature $T_{e,ss}$	Heating time t_H
I	< 150	$\theta < 1.5$	< 10	Biomass processing	$T_a \left(\frac{\alpha}{\beta} + 1 \right) = \frac{\sigma \left(\frac{V}{L} \right)^2 L_{th}}{T_a + \frac{V}{L} \frac{L_{th}}{h}}$	$\frac{t_0}{\beta} = \frac{\rho C_p L_{th}}{h}$
II	150 – 300	$1.5 < \theta < 2$	< 14	Hydrodeoxygenation of biomass, hydrogenolysis and hydrocracking of plastics	$T_a \left(\frac{\alpha}{\gamma} + 1 \right)^{\frac{1}{4}} = T_a \left(\frac{\sigma \left(\frac{V}{L} \right)^2 L_{th}}{e \Sigma T_a^4} + 1 \right)^{0.25}$	$= \frac{\frac{t_0}{4(\alpha + \gamma)^{\frac{3}{4}} \gamma^{\frac{1}{4}}}}{\rho C_p L_{th}} = \frac{1}{4 \left(\sigma \left(\frac{V}{L} \right)^2 L_{th} + e \Sigma T_a^4 \right)^{0.75}} e^{0.25 \Sigma^{0.25}}$
III	300 – 550	$2 < \theta < 3$	< 35	CO ₂ hydrogenation, NH ₃ cracking, and low temperature pyrolysis	$T_a \left(\frac{\alpha}{\gamma} + 1 \right)^{\frac{1}{4}} = T_a \left(\frac{\sigma \left(\frac{V}{L} \right)^2 L_{th}}{e \Sigma T_a^4} + 1 \right)^{0.25}$	$= \frac{\frac{t_0}{4(\alpha + \gamma)^{\frac{3}{4}} \gamma^{\frac{1}{4}}}}{\rho C_p L_{th}} = \frac{1}{4 \left(\sigma \left(\frac{V}{L} \right)^2 L_{th} + e \Sigma T_a^4 \right)^{0.75}} e^{0.25 \Sigma^{0.25}}$

IV	550 – 1100	$3 < \theta < 5$	< 170	CH ₄ reforming, high temperature pyrolysis, ethane and propane dehydrogenation	$T_a \left(\frac{\alpha}{\gamma} \right)^{\frac{1}{4}} = \frac{\sigma^{0.25} \left(\frac{V}{L} \right)^{0.5} L_{th}^{0.25}}{e^{0.25} \Sigma^{0.25}}$	$t_0^{\frac{3}{4}} = \frac{\rho C_p L_{th}^{0.25}}{4 \alpha^{0.75} \gamma^{\frac{1}{4}} \left(\frac{V}{L} \right)^{1.5} e^{0.25} \Sigma^{0.25}}$
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Temperature range I includes reactions related to biomass processing, such as fructose dehydration. Such processes frequently involve liquids (for e.g. water, ethyl acetate, methyl isobutyl ketone)[104, 105] that are typically governed by forced convective heat transfer from the element to the fluid due to the liquid's smaller kinetic viscosity compared to gas (water $\sim 10^{-6} \text{ m}^2/\text{s}$ and gas $\sim 10^{-5} \text{ m}^2/\text{s}$). Also, liquids like water typically exhibit higher $Nu \sim 10$ -53 and $Pe \sim 0.3$ -10 compared to gases ($Nu \sim 4$ and $Pe \sim 0.05$ for He). Despite $\frac{Nu}{Pe}$ being an order of magnitude smaller for liquids compared to gases, liquids' β is higher due to the ratio of the volumetric heat capacities being 3-4 magnitudes larger. For, $\theta < 1.5$ and $< 10 \text{ W}$, radiation is negligible as $\alpha, \beta \gg \gamma$, and Eq. 2.20 is linear in θ and dependent only on α and β . Solving Eq. 2.20 gives an estimate of the heating time scale for the element ($t_H \sim 1.5 \text{ s}$ for temperature range I for water assuming $r = 11 \text{ mm}$, $U_{in} = 30 \text{ ml/min}$). For ranges II-III, which involve gas-phase chemistry, we can only ignore the conduction to the gas (dependence on α and γ). For range IV, Eq. 2.20 is also only dependent on α and γ but the input power is high, making $\alpha \gg \gamma$. For instance, when 170 W is applied to the carbon fiber element, $t_H = 0.46 \text{ s}$ and $t_{ss} = 2.3 \text{ s}$. [106] Similarly, in temperature ranges III and II, $t_H \sim 1 \text{ s}$ and $\sim 6 \text{ s}$, assuming 35 W and 14 W, respectively. All analytical equations in Table 2.3 agree well with CFD with average error $\sim 25 \%$ (refer

to Figure A.9 for parity plots). Overall, these relatively short times indicate the ability of the system to respond fast to transient operations.

Similar conclusions can be derived from the element's steady state temperature. It increases with an increase in element's electrical conductivity, thickness, and voltage, and decreases with an increase in the element's length. The voltage and element's length are the dominant parameters. For temperature range I, the steady state temperature increases as h decreases. For temperature ranges II-IV, emissivity is a key parameter; a decrease in emissivity leads to an increase in temperature.

2.4.4 Pulsed Joule heated reactors

Rapid pulse Joule-heated reactors have recently been proposed for higher energy efficiency and performance.[75, 76] The element is subjected to cycles of heating (voltage on) followed by cooling (voltage off). This process generates an oscillatory temperature profile, referred to as a 'pulse'.

Figure A.10 shows the voltage pulse applied to the element and the associated temperature profile at the element's center point. The temperature rapidly increases during heating due to the resistive power supplied (~ 500 W). The radiative loss increases, explaining the decreasing heating rate at higher temperatures (a decreasing slope or effective heating rate). During cooling, the temperature gradually decreases as cooling due to conduction and radiative losses from the element. The reduction in radiation leads to a slower cooling rate with time. The conductive loss to the gas remains approximately constant throughout the cycle. As the voltage V increases, the resistive power also rises, following $P = \frac{V^2}{R}$, which in turn elevates the peak

temperature. The duration of heating and cooling parts of the cycle (duty) also affects the temperature.

As detailed in Figure A.11, isotherms shift downwards as the element's temperature increases and upwards as the element's temperature decreases, following the same trend as discussed in continuous Joule-heated reactors.

Figure 2.10 shows the maximum velocity vs. axial position at various times (detailed in Figure A.12) of a given pulse. During heating, the velocity keeps on increasing due to continuous heating as the gas flows over the element. Small peaks in the velocity before the element, indicative of reverse flow, are also observed. During cooling, the velocity decreases, leading to a pressure increase and upward flow. This behavior is ascribed to substantial reverse flows (refer to Figure A.13 and Figure A.14 for axial flow velocity). The significant variations in the maximum velocity suggest changes in the residence time, which will affect chemical reactions.

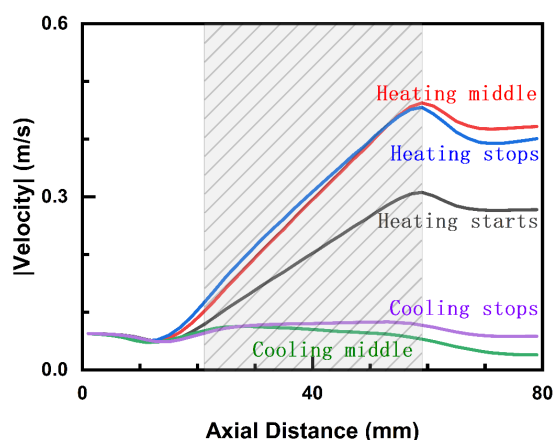


Figure 2.10: Maximum velocity normal to the reactor axis vs. axial position at 90 mL/min during a pulse. The shaded region denotes the heating element.

The thermal boundary expands during heating and contracts during cooling, as seen in Figure A.15. These results align with the isotherms reported by *Dong et al.*[76]. The impact of dynamics on the Nu number is shown in Figure 2.11. Nu declines gradually during heating and part of the cooling until a minimum before start rising again. Figure 2.11 indicates that pulsing enhances heat transfer from the element to the gas due to increased Nu number. This may have to do with the dynamic nature of the thermal boundary layer and manifests how dynamic operation intensifies the heat transfer rate.

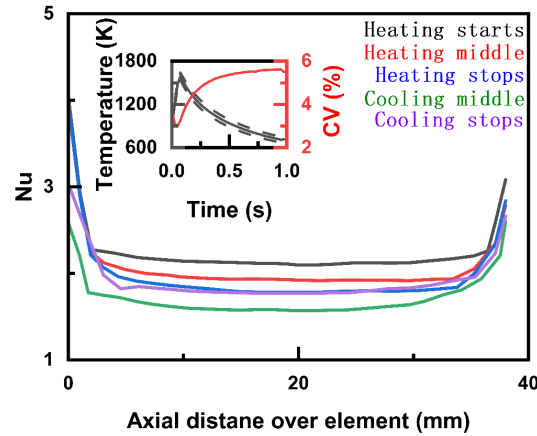


Figure 2.11: Nusselt number vs. distance from leading edge of the element at various times. The inset shows the average element's surface temperature (solid line) with the standard deviation interval (dashed lines) for a pulse of 50 V for 50 ms (heating) and 950 ms (cooling) with He inlet flow rate of 90 mL/min. The temperature variation is also shown.

2.5 Conclusion

We developed a CFD model for a Joule-heated reactor consisting of carbon fiber paper heated by an externally applied voltage. The model is in excellent agreement with experimental data. High and uniform temperatures of the CFP can be

achieved with a low power input due to its high thermal and electric conductivity. Most of the power is radiated away from the element in this configuration, and the gas flowing by is hot only near the heating element. This implies that undesired gas phase chemistry can be suppressed in this configuration. At typical laboratory scales, we found flow recirculation induced by buoyancy. The reverse flow influences the temperature isotherms. Above a minimum velocity, the reverse flows are suppressed. The Nu for the heat transfer from the heating element to the gas reveals a U-shaped trend with a low magnitude indicative of free convection and enhanced transport near the leading and trailing edges of the element due to recirculation.

We also developed a 0D energy balance model to predict the various timescales rapidly. The model is in decent agreement with the CFD model. Analytical expressions were derived under certain assumptions for the steady state temperature and time scale controlling heating. These reveal the dependency on various design parameters. We have identified the voltage and the element's length, electrical conductivity, and thermal conductivity as the dominant design factors. The volumetric heat capacity and the thermal conductivity of the fluid influence the heating rate and time to reach a steady state in low-temperature reactions involving liquids. Joule-heated reactors showcase high heating rates and a short time (seconds or shorter) to steady state and, thus, are suitable for fast transient operation. Finally, rapid pulsing enhances the heat transfer and tunes the residence time due to strong reverse flows.

Chapter 3

JOULE-HEATING MATERIALS FOR ADVANCED CHEMICAL MANUFACTURING

3.1 Contributions

This chapter contains published work,[44] performed for the completion of this thesis. This work was performed by thesis' author.

3.2 Introduction

Supporting the growing global population with energy and essential products has led to increased fossil fuel consumption and emissions.[10] The chemical industry alone contributes over 3.3 Gt CO_{2eq.} annually, primarily due to the energy-intensive nature of endothermic reactions, separations, heat exchangers, and compressors.[2] Traditional thermal processing methods rely on external heat sources, resulting in slow response times, high thermal inertia, large systems, and significant energy losses. Electrocatalysis, microwaves, plasmas, inductive heating, and Joule heating can significantly reduce emissions while enhancing energy and process efficiency. Among these technologies, Joule-heated (or Ohmic) systems offer a theoretical energy efficiency of ~100%. Microwave and inductive systems can achieve efficiencies of >90% and ~85%, respectively, while plasma-powered systems generally exhibit lower energy efficiencies.[31, 38] Joule-heated systems provide a more straightforward and scalable approach, as they directly heat a resistive material (the Joule heating element). In contrast, other electrified systems require complex power supply designs

for effective scale-up.[30] These systems offer extremely rapid heating rates ($\sim 30,000$ °C/s), reasonable cooling rates ($\sim 1,000$ °C/s), high thermal efficiency, and localized heating capabilities. These heating and cooling rates enable unique dynamic programmability of the system's temperature. Often referred to as pulsed Joule heating, this capability allows precise interruption of reactions, particularly chain reactions involving multiple consecutive reaction intermediates.[76, 107] They are suitable for modularized and distributed manufacturing, which can be applied to utilizing fossil fuels and other feedstocks in remote and offshore locations.[43, 108] Furthermore, their ability to be integrated with intermittent renewable energy sources and retrofit existing chemical infrastructure makes them attractive.

Recent studies have explored various Joule-heated materials, including metals (e.g., tungsten, molybdenum),[70] alloys (e.g., FeCrAl, stainless steel),[83, 109] carbon- and silicon carbide-based materials (carbon fiber paper (CFP) and SiC).[75, 108, 110] Wires, foams, monoliths, screens, pellets, fibers, and tubes, have been investigated.[108, 111, 112] This variability in materials and structures underscores the lack of fundamental principles for material selection. Trade-offs in performance should be expected. For example, while CFP and SiC exhibit superior temperature uniformity and higher heating rates than alloys,[75, 113] metals and alloys require lower power to reach comparable temperatures.[83] However, the lack of a systematic framework for material selection, trade-offs between thermal efficiency and power requirements, and uncertainty in structural stability under high electric fields present challenges in process design and scalability.

This study introduces performance metrics for Joule-heated systems and predictive models for material selection and system design, such as chemical reactors,

heat exchangers, and unit operations. Parametric computational fluid dynamics (CFD) simulations provide power-law correlations that link key performance metrics to material properties, enabling accurate performance predictions across diverse operating conditions. By analyzing the interdependence of electrical and thermal properties using machine learning (ML), we provide a systematic framework for selecting materials for various chemical processes. We explain the experimental observations reported in the literature on Joule-heated systems. We demonstrate that the maximum heating rate is an intrinsic material property. Operating at high heating rates significantly enhances startup efficiency—defined as the fraction of energy stored in the material during heating relative to the total energy input—approaching 100%. Yet, practical power supply limitations may arise. Finally, we evaluate the effective properties of structured heating elements and power dissipation as a function of porosity using multiscale modeling techniques. These insights contribute to developing scalable, efficient, and structurally stable Joule-heated systems for industrial applications.

3.3 System description, computational methods, and material performance metrics

Figure 3.1 shows the geometry of a Joule-heated system considered here for illustrative calculations. The system consists of a thin, long tape connected to two copper electrodes in the middle of a tube, with gas flowing along the tape's long dimension.

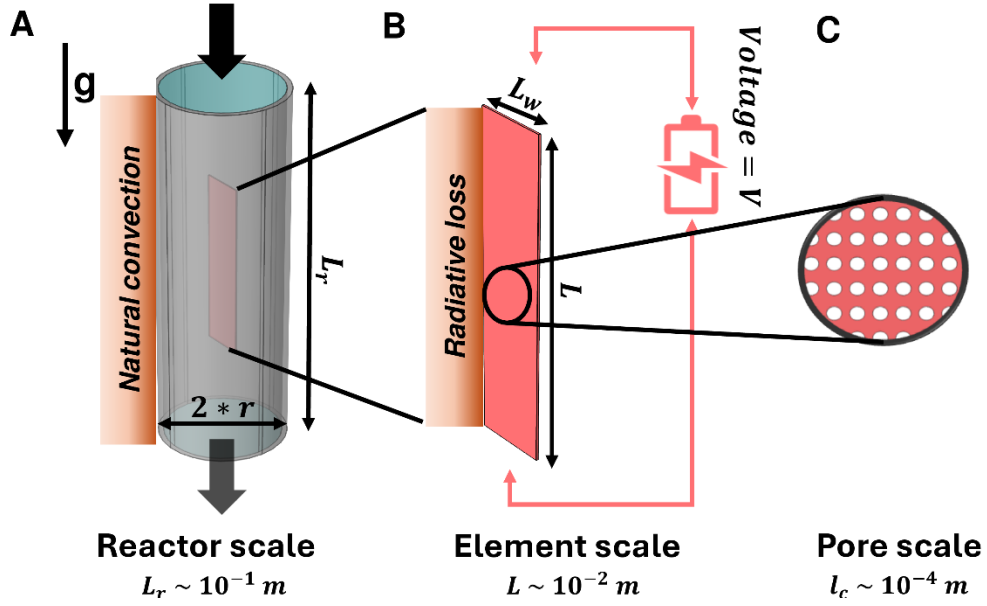


Figure 3.1: Schematic of the Joule-heated system modeled in COMSOL with associated boundary conditions. The nominal sizes include a heating tape of length (L), width (L_w), and thickness (L_{th}), in a quartz tube of radius (r), and length (L_r) in continuous gas flow. This geometry reproduces a recently introduced experimental system.[75] V represents the constant voltage difference applied to the Joule heating element.

We model the energy transport in the solid heating element and flow and energy conservation equations in the fluid flowing along it, as well as the heat transfer between them accounting for all interfaces, in detail. We solve the electric current equations to get the current density J , the electric field intensity E , and the resistive power density Q_{eh} dissipated into the material[85, 114] (heat generation term in the energy equation). The energy equation, electric current equation, continuity equation for compressible fluids, and Navier-Stokes (flow) equations are solved[114] using the COMSOL Multiphysics software to evaluate the spatial temperature field.[115, 116] We employ the AC/DC, heat transfer, and laminar flow modules and solve the time-dependent, three-dimensional (3D) equations due to the non-axisymmetric Joule

heating element and non-symmetric vortices[117], using the inbuilt finite element solvers (for details, refer to Section B.1).

The boundary conditions follow prior work (Figure 3.1A).[117] Briefly, all Joule heating element surfaces except the terminals are electrically insulated. The tangential component of the electric field and the normal component of the electric displacement at the element-gas interface are considered continuous. Heat loss due to natural convection outside the quartz tube and radiation loss from all element surfaces are accounted for (Figure 3.1B). The element's initial temperature (T_{in}) is 20 °C. The gas inlet temperature (T_g^{in}) is 20 °C; zero gradient boundary conditions are applied at the outlet. A zero gradient for pressure and no-slip boundary conditions are imposed at the tube wall. A zero gradient and constant velocity are used for the pressure and velocity at the inlet, respectively. At the outlet, the velocity has zero gradient, the backflow is suppressed, and the pressure is constant (atmospheric). Mesh dependency tests ensured discretization-independent results.[117] A fine general physics mesh inside the Joule-heating element and a normal one for the quartz tube and the fluid around the element is used. The effect of the applied voltage and heating element structure, specifically its length (L) and the volume-to-surface area ratio (λ) (for details refer to Section B.2), are considered. λ is proportional to L_{th} for a heating tape, wire diameter for an electrical wire, and cylinder length for wash-coated cylinders.

Table 3.1: Intrinsic properties of various materials.[81, 115, 117-125]

Material	σ @ 20 °C [S/m]	ρ [kg/ m ³]	C_p @ 20 °C [J/(kg* K)]	κ [W/(m* K)]	Melti ng Point °C	Tensil e stren gth [MPa]	Therm al Expans ion coeffici ent [10-6/ °C]	Jma x [A/m 2]
CFP*	2 * 10 ³	452	990	400	3900	250	1.5	-
SiC	1.8 * 10 ³	3210	750	120	2800	345	4	5 * 10 ⁶
FeAlCr	7.1 * 10 ⁵	7200	510	11	1700	350	11	-
Nichrome	6.7 * 10 ⁵	7900	500	13	1390	750	13	-
Stainless steel	1.4 * 10 ⁶	7860	500	16.3	1400	860	16	5 * 10 ⁶
Chromium	8.3 * 10 ⁶	7190	461	69.1	1860	413	6.2	3 * 10 ⁵
Molybden um	1.9 * 10 ⁵	10220	217	138	2617	324	5	3 * 10 ⁵
Tungsten	1.8 * 10 ⁷	19300	134	164	3370	980	4.5	3 * 10 ⁷
Copper	2.9 * 10 ⁷	7764	385	400	1083	210	17	1 * 10 ⁷
Aluminum	3.5 * 10 ⁷	3640	890	25	660	180	23	5 * 10 ⁹
Titanium	2.4 * 10 ⁶	4500	523	17	1670	220	8.6	4.5 * 10 ⁶
Nickel	1.6 * 10 ⁷	8800	460	60.7	1455	317	13.3	1.5 * 10 ⁶
FeCr	1 * 10 ⁶	7200	475	22.5	1360	320	11	-
FeCrNi	1.5 * 10 ⁶	7850	500	17.5	1500	1035	16	-
NiCr	1.1 * 10 ⁶	8400	420	12	1400	655	13	-

We evaluate various Joule heating element materials and key properties e.g., electrical conductivity (σ), density (ρ), heat capacity (C_p), emissivity (e), and thermal conductivity (κ), listed in Table 3.1.[81, 115, 117-125] We compute performance metrics, including the heating rate (R_h), which expresses how fast the temperature rises upon turning on the voltage; the cooling rate (R_c), which is the rate of temperature decline upon turning the voltage off; the steady-state temperature (T_{ss}), which controls the rates of physical and chemical processes; the time to reach steady state (t_{ss}), which dictates the system's dynamic behavior; temperature and current density uniformity using the coefficient of variation (CV); and the startup efficiency, indicating the fraction of energy stored in a material during heating vs. being lost to the environment; it is a valuable metric when a system operates dynamically.[96, 117] The maximum attainable heating rate ($R_{h,max}$) is also evaluated, which is later proven to be an intrinsic material property. All performance metrics are defined in Section B.2.

The power supplied to a Joule-heated element is

$$\text{Power: } P \text{ (W)} = I * V = \frac{V^2}{R} = I^2 R \quad (3.1)$$

Here R is the resistance of the material, V is the voltage, and I is the current. The maximum attainable heating rate depends on the maximum allowed electric current density J_{max} (also referred to as the current density safety limit) in a material achieved at the maximum operating voltage

$$\begin{aligned} \text{Maximum voltage: } V_{max} &= I_{max} * R = I_{max} * \left(\frac{L}{\sigma A} \right) = \left(\frac{I_{max}}{A} \right) * \left(\frac{L}{\sigma} \right) \\ &= \frac{J_{max} * L}{\sigma} \end{aligned} \quad (3.2)$$

Here A is the element's cross-sectional area.[81] Above J_{max} , material atoms can undergo flashover (movement across insulated surfaces) due to electric current forces, resulting in hotspots or thermal cracks, a phenomenon known as electromigration.[126] At J_{max} , the number of unstable conduction band electrons (hot electrons) increases, promoting electron movement across the surface and bulk. This enhances the energy release from surface-trapped hot electrons, reducing the surface's effectiveness in holding electrons.[126] J_{max} depends on bulk resistivity, making J_{max} higher for superconductors and high-performance semiconductors. J_{max} is $\sim 10^7$ A/cm² for several materials, lower for Cr and Mo, and higher for Al (Table 3.1). Given that J_{max} is not known for many materials, this study considers a constant, moderate value when comparing materials, as the overarching conclusions do not depend on the specific values. We implemented Principal Component Analysis (PCA) and a clustered covariance matrix using the Python library scikit-learn to identify material properties influencing performance metrics.[105, 127]

Aside from intrinsic materials properties, performance metrics depend on the macro- and meso-structure of structured or porous heating elements. Resolving each tiny feature of a material is beyond current computational resources. Homogenization theory and volume averaging leverage length scale disparities to estimate effective properties typically through calculations in a unit cell, the smallest cell whose periodic translation captures the variation in materials structure and/or properties (Section B.3).[128-130] These methods can estimate effective permittivity, thermal conductivity, and volumetric power absorbed of multiphase microwave systems.[131-133] For Joule-heated systems, we consider elements with variable porosity (φ), having fully penetrated pores of a characteristic length l_c ($O(100 \mu m)$), significantly

smaller than the element's overall length L ($O(1\text{ cm})$) (Figure 3.1C). This length scale separation allows coarse-graining of the governing equations.[134] We apply volume averaging to calculate the effective electrical conductivity σ_{eff} and volume-averaged resistive power density $\langle Q_{eh} \rangle$ and homogenization for estimating the effective thermal conductivity.[132] The techniques are well known and are applied here to resistive heating. Details regarding the unit cell and COMSOL calculations are given in Section B.3. All average values were obtained using COMSOL's in-built volume averaging function.

3.4 Results and discussion

3.4.1 Parametric analysis and material comparison

Starting with nominal values of CFP, we evaluated the performance metrics through CFD simulations and fitted a power law model to quantify their dependence on each parameter (Figure 3.2; Table B.1 in Section B.4 shows fitting statistics). The fitted exponents are non-integers due to the temperature dependence of heat capacity and electrical conductivity and the heat losses from the element edges.

For a given material, increasing the applied voltage enhances the heating rate quadratically by increasing the resistive heating power. Conversely, a longer element reduces the heating rate by diminishing the resistive heating power generated (Figure 3.2A). At constant voltage and geometry, materials with higher electrical conductivity exhibit higher heating rates due to greater resistive power generation. In contrast, materials with higher density or heat capacity lower the heating rate, as such materials require more energy to be heated for a given mass. The volume to surface area ratio, emissivity, and element's width exert negligible influence on the resistive power

generation for a fixed mass and, thus, on the heating rate. These findings suggest that the heating rate is governed by the electrical conductivity, volumetric heat capacity, and the voltage applied, with the element's geometry (except length) or shape playing a minor role

$$\text{Heating rate } \left(\frac{K}{s}\right): R_h \sim \frac{\sigma^{0.91} \lambda^{0.22} V^{2.04}}{\rho^{0.75} C_p^{0.7} e^{0.22} L^{1.5}} \sim \frac{\sigma V^2}{\rho C_p L^2} \quad (3.3)$$

Here and below, the first expression shows the fitted exponents, which are rounded off to the nearest integers in the second expression. Consequently, the same heating rate can be achieved across a monolith, tube, foam, or heating tape made of the same material (having the same nano-porosity) and length.

Figure 3.2B indicates that the steady-state temperature, T_{ss} , parallels the heating rate: a higher voltage and electric conductivity achieve higher T_{ss} . But also, a noticeable difference: T_{ss} depends strongly on the volume-to-surface-area ratio and, thus, on the geometry of the heating element due to heat losses. Unlike the heating rate, the volumetric heat capacity has a negligible effect on T_{ss}

$$\text{Steady state temperature } (K): T_{ss} \sim \frac{\rho^{0.17} C_p^{0.17} \sigma^{0.87} e^{0.03} \lambda^{0.8} V^{1.7}}{L^{1.32}} \sim \frac{\sigma \lambda V^2}{L} \quad (3.4)$$

Here, $\frac{\lambda}{L}$ represents the cross-sectional area over the total external surface area of the element and quantifies the geometrical efficiency of resistive heating. It directly correlates with the current generation and the resistive power dissipation: a higher value suggests enhanced power generation within a given volume.

Figure 3.2C shows that decreasing the volume-to-surface area ratio reduces the time to steady state, t_{ss} , due to storing less energy in the material. The system reaches steady state faster for a lower steady-state temperature or a higher heating rate

$$\text{Time to steady state } t_{ss} (s) \sim \frac{T_{ss}}{R_h} \sim \frac{\rho^{0.92} C_p^{0.88} e^{0.15} L^{0.18} \lambda^{0.58}}{\sigma^{0.04} V^{0.34}} \sim \frac{\rho C_p \lambda L}{V} \quad (3.5)$$

Here, λL represents the length-averaged cross-sectional area of the element. It characterizes the geometric efficiency of encapsulating volume while minimizing external surface area. A higher λL value indicates a smaller external surface area and reduced heat loss. The impact of all material properties and operating conditions on the time to steady state can be explained by their impact on the heating rate and steady-state temperature. For example, materials with lower volumetric heat capacity maintain a similar steady-state temperature (for the same operating conditions) but achieve a higher heating rate, further reducing the time to steady-state. Increasing the voltage raises the steady-state temperature but drastically enhances the heating rate, resulting in a shorter time to steady state.

Figure 3.2D presents the cooling rate dependence from an initial 1200 °C (results are independent of the initial temperature in the range of 500–1200 °C). Among the parameters, the volume-to-surface area ratio, followed by heat capacity, density, and emissivity, influences the cooling rate the most.

$$\text{Cooling rate } \left(\frac{K}{s}\right): R_c \sim \frac{1}{\rho^{0.27} C_p^{0.27} \lambda^{0.56} e^{0.16}} \sim \frac{1}{\lambda} \quad (3.6)$$

Overall, the material dependence is weak because cooling is primarily governed by convective and radiative losses, which are smaller in magnitude than the resistive heating power.

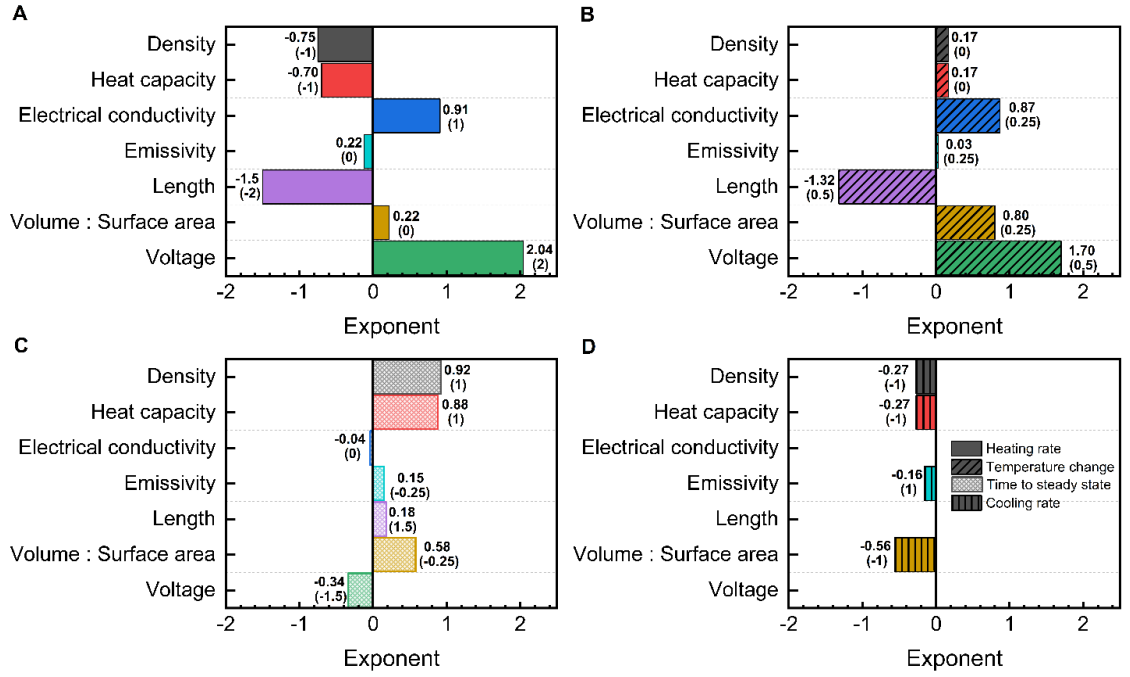


Figure 3.2: Performance metrics correlations. The performance metric is approximated as a power law model, $\sim x^a$, where x is the varying property, geometric factor, or voltage and a is the exponent. Performance metric: (A) Heating rate, (B) element spatial average (overbar) steady-state temperature increase over inlet temperature ($\overline{T_{ss}} - \overline{T_{in}}$), (C) time to steady state, and (D) cooling rate. A non-porous material is considered. Nominal parameters include He flow rate of 90 sccm, $L = 38$ mm, $L_w = 8$ mm, $L_{th} = 0.0525$ mm, $V = 3.75$ V, $e = 0.12$, and other material properties of CFP ($\rho = 452$ kg/m³, $C_p = 1000$ J/kg*K, and $\sigma = 6000$ S/m). Numbers alongside the bars indicate the fitted exponents, while numbers in parentheses represent the theoretical exponents from a simple, isothermal energy balance.

These exponents enable efficient exploration of a high-dimensional space. For instance, to increase the heating rate by 4x, the voltage can be doubled, or the length can be reduced by 2x. Similarly, longer elements can maintain comparable performance by increasing the voltage. Eq. B.8 illustrates the (0D) isothermal element transient energy balance, which captures the interplay of multiple variables. Analytical

expressions can be derived in limiting cases, given knowledge of flow and heat transfer within a system, such as transport correlations. These exponents are also shown in Figure 3.2 in parentheses. As expected, steady-state temperature predictions (Eq. 3.4) are in good agreement with CFD for various materials (Figure B.2). The theoretical exponents differ from the numerical ones due to the isothermal assumption, constant properties, and temperature-dependent heat loss mechanisms (conductive losses at lower temperatures and radiative losses at higher temperatures). The assumption of isothermal behavior does not hold for all materials (as discussed in Section 3.2); significant temperature gradients throughout the element's volume may exist, thereby affecting material properties, such as electrical conductivity and heat capacity, and thus, performance metrics. This rationalizes the deviation of the fitted exponents for electrical conductivity from the analytical ones for the spatially averaged steady-state temperature and time to steady state. Specifically, the fitted exponent exceeds the analytical one because the electrical conductivity typically decreases with increasing temperature.

The temperature uniformity is a key performance metric. Figure B.3A illustrates that as the voltage increases, both the temperature and the temperature non-uniformity (ΔT) rise. Figure B.3B quantifies the impact of material properties, size, and applied voltage on the temperature uniformity. Figure 3.2B and Figure B.3B demonstrate that parameters controlling the steady-state temperature also impact the material's temperature uniformity. Highly thermally conductive materials, such as graphene ($\kappa \sim 4000 \text{ W}/(\text{m}\cdot\text{K})$) and CFP ($\kappa \sim 400 \text{ W}/(\text{m}\cdot\text{K})$) have a negligible coefficient of variation (CV), of $< 10^{-8}$ and $\sim 10^{-3}$, respectively, ensuring an isothermal surface under typical conditions.

Eq. 3.7 shows the minimum thermal conductivity (κ_{crit}) needed to ensure an isothermal element (derived in Section B.5).

$$\text{Critical thermal conductivity } \left(\frac{W}{m \cdot K} \right) : \kappa_{crit} = \frac{Nu * \kappa_g}{\varepsilon} \quad (3.7)$$

Here Nu is the Nusselt number, κ_g is the thermal conductivity of the carrier gas, and ε is a small number. Assuming $\varepsilon = 0.01$ and utilizing an empirical correlation to calculate Nu,[101, 117] we estimated κ_{crit} of a vertical heating tape. $\kappa > 100 \text{ W/(m}\cdot\text{K)}$ can ensure isothermicity of a vertical heating tape of length $\sim 4 \text{ cm}$ operating in He between 700 and 1700 K (Figure B.4). We estimate that the cylindrical walls of prior work[83] require $\kappa > 500 \text{ W/(m}\cdot\text{K)}$ to be isothermal due to longer lengths and higher conductive heat losses. κ_{crit} increases with the element's length, reactor's radius, carrier gas density, volumetric heat capacity, and thermal conductivity, and decreases with increasing the dynamic viscosity of the carrier gas. κ_{crit} will rise when carrying out endothermic reactions due to the element providing more energy (enhanced effective heat loss). Metal alloys and ceramics of low thermal conductivity are expected to exhibit temperature gradients even for short elements.

3.4.2 Material stability and operational limits

Beyond the above performance metrics, material stability under extreme operating conditions is crucial for the long-term viability of a system. High thermal conductivity ensures an isothermal system, preventing fractures during rapid temperature changes. Additionally, materials must also resist thermal shock and be chemically inert. Consequently, operational limits are dictated by the maximum current density, melting point, thermal expansion coefficient, mechanical strength, and chemical inertness. Next, we examine how these intrinsic properties influence the

heating rate; the minimum time to reach a steady state and the maximum steady state temperature are analyzed in Section B.6.

The maximum heating rate is determined from Eqs. 3.1 and 3.3 so that the maximum current density is J_{max} .

$$\text{Maximum heating rate } \left(\frac{K}{s}\right): R_{h,max} = \frac{J_{max}^2}{\sigma \rho C_p} \quad (3.8)$$

It is an intrinsic material property (independent of voltage and overall geometric features; see also below). Figure 3.3A illustrates the maximum attainable heating rate (Eq. 3.8) for various materials, assuming temperature-independent electrical conductivity, density, and thermal heat capacity, and $J_{max} = 10^7 \frac{A}{m^2}$. [81] Small lab-scale elements ($0.1\text{-}1 \text{ cm}^3$) can achieve these heating rates. However, as the size increases, the power demand increases, and it becomes essential to consider the maximum power available. Carbon-based materials and SiC show three orders of magnitude higher maximum heating rates than FeAlCr and stainless steel due to their lower electrical conductivity and volumetric heat capacity. In contrast, metals like copper and aluminum, with high electrical conductivity, exhibit lower maximum heating rates but require less power input and longer heating times.

To streamline material selection, we applied machine learning feature analysis to 15 materials commonly used in Joule-heating (Table 3.1). Seven parameters were analyzed: electrical conductivity, density, specific heat capacity, thermal conductivity, melting point, tensile strength, and thermal expansion coefficient along with maximum heating rate (predicted in Figure 3.3A). Figure B.6A presents PCA results, showing that four properties account for over 90% of data variance and five for more than 95%. Figure B.6B displays a scatter plot of material properties on the principal component plane, highlighting four distinct property groups: group 1: thermal

expansion coefficient; group 2: tensile strength; group 3: density, electrical conductivity, melting point, and maximum heating rate; and group 4: heat capacity and thermal conductivity. Groups 1 and 2 are orthogonal and independent of each other. Similarly, group 3 is orthogonal to group 2, confirming the separability and independence of key material properties. Figure B.6C presents the covariance matrix, highlighting interdependencies among material properties. Density, specific heat capacity, and tensile strength show strong correlations: density negatively correlates with the specific heat capacity (higher density implies lower heat capacity) but positively correlates with the tensile strength (higher density enhances strength).

Figures B.6B and 6C identify four independent intrinsic properties: maximum heating rate, melting point, thermal conductivity, and thermal expansion coefficient. Figure 3.3B compares commonly used Joule-heating materials based on these properties. The x-axis represents the maximum heating rate (calculated using Eq. 3.8) and the y-axis shows the melting point. The materials are classified into operating temperatures corresponding to select chemistries chosen for illustration: the blue region for NH_3 cracking, low-temperature plastics recycling, and biomass-based reactions; the orange region for ethane and propane cracking; and the red region for methane reforming and ethane/naphtha steam cracking. For structural stability, the steady-state temperature must remain below two-thirds of the melting point ($T_{\text{melt}} > 3/2 T_{\text{ss}}$).

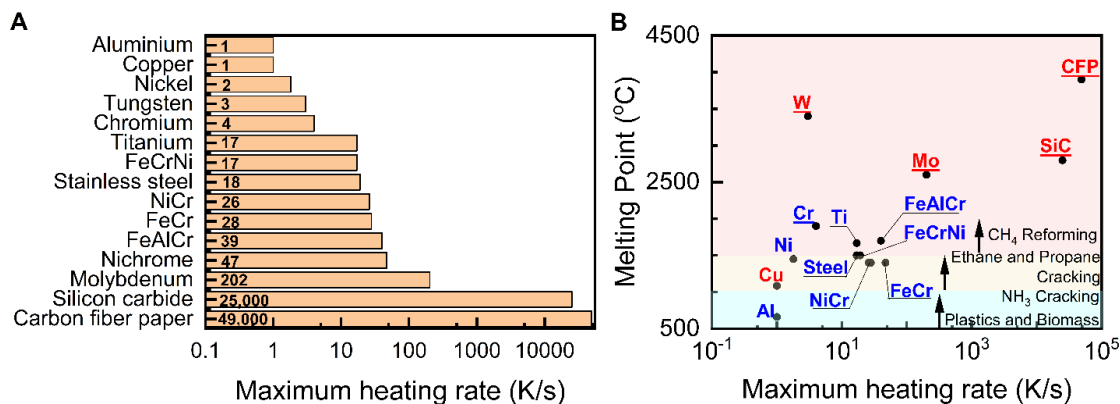


Figure 3.3: Intrinsic material properties interdependency study. (A) Maximum attainable heating rate without causing electromigration. Numbers indicate the heating rate in K/s. (B) Material comparison graph based on the top 4 intrinsic material properties. Materials in red have $> 100 [W/(m \cdot K)]$ and in blue have $< 100 [W/(m \cdot K)]$; underlined materials possess a low thermal expansion coefficient). The graph is color-coded by the operational temperature of various reactions marked with arrows. The voltage per unit length are listed in Table B.2.

Materials in red have high thermal conductivity, ensuring isothermal surfaces ($CV < 1\%$ for $L < 4 \text{ cm}$; see Figure B.4). Underlined materials can be potentially stable under dynamic operation, such as rapid temperature pulsing, due to their low thermal expansion coefficients. Aluminum is suitable only for low-temperature applications, such as those involving plastics or biomass reactions, due to its low melting point and slow heating. Alloys perform well for midrange temperatures (e.g., ethane and propane cracking). Carbon materials have high melting points, high heating rates, high thermal conductivity, and low thermal expansion, followed by molybdenum (Mo), although Mo has a higher cost. Finally, tensile strength correlates positively with density, inversely affecting the maximum heating rate. This trade-off highlights the importance of materials like SiC, which offer both structural stability and high heating rates, for demanding applications.

Recent experimental studies have exposed some of these points, but no previous studies have provided a roadmap for material selection. For instance, *Porsin et al.*[69] utilized tungsten wires (W) for methane pyrolysis due to W's high melting point and high thermal conductivity. However, W's high electrical conductivity leads to higher currents and power losses through electrical connections, and the maximum current density[81] restricts the achievable temperatures (Figure B.5). W also forms tungsten carbide in hydrocarbon environments or can be oxidized. Mo and nichrome wires have also been used for converting light hydrocarbons to alkenes, but W is superior.[70] Mo reacts with oxygen above 400 °C. To prevent such oxidation, metals are typically coated with protective layers, which can alter the material's physical properties, especially the electrical conductivity.[135-137] *Wismann et al.*'s[77, 79, 83] FeCrAl-alloy tubes exhibited high axial temperature gradients ($\Delta T > 300\text{ K}$ over 40 cm). Ceramics, often used for CO oxidation due to their resistance to oxidation and corrosion,[71, 80] have high volumetric heat capacity and a large surface area, requiring significantly more power, which results in lower heating rates and steady-state temperatures. Similarly, Si-doped SiC porous foams offer high surface area but demand significant power ($P > 300\text{ W}$ for $T > 1000\text{ K}$) to achieve high temperatures due to low electrical conductivity.[42, 113, 138] *Yu et al.*[75] demonstrated CFP's effectiveness in methane dry reforming, achieving high heating rates and efficient catalyst utilization. Rapid pulsing gave higher conversions and selectivity.[75, 76] These properties make CFP ideal for high-temperature applications with lower power requirements and for dynamic operation, allowing for quick adjustment to fluctuations in energy supply and demand. In initial experimental work, we have found CFP to possess excellent chemical inertness; however, its long term, very high temperature

stability under oxidative conditions remains to be investigated.[28, 41, 75] Overall, the experimental observations are rationalized by our theoretical and computational work.

The maximum deliverable power by a material of a certain volume is equal to the power required to attain maximum heating rate, and is given by:

$$\begin{aligned} \text{Power to attain maximum heating rate (W): } P &= \frac{\sigma V_{max}^2 A}{L} \\ &= \frac{J_{max}^2 * V_{elem}}{\sigma} \end{aligned} \quad (3.9)$$

Here V_{elem} is the volume of the element. The maximum deliverable power density of commonly used materials is shown in Figure 3.4. The difference between the power required to maintain the operating temperature (more details in Section B.8) and the maximum deliverable power represents the material's capacity to supply additional power for the heat of reaction, latent heat, or other power demands. A high maximum deliverable power density implies that a smaller heating element of a material are needed in the system. For instance, a system requiring 1000 W can be designed either using 0.02 cm^3 of CFP or using 10 cm^3 of nichrome. This eases system design and boosts economics by minimizing material costs.

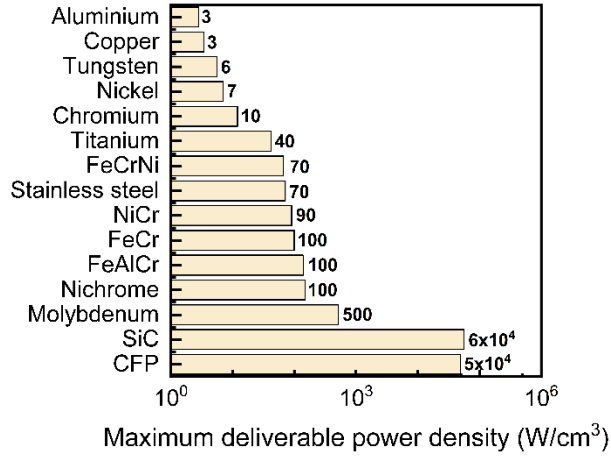


Figure 3.4: Maximum deliverable power density for various materials. The numbers represent a rounded value in W/cm³.

Further, the maximum power is limited either by the maximum current density or the available one

$$\text{Maximum power (W): } P_{max} \leq \min \left\{ \frac{J_{max}^2 * V_{elem}}{\sigma}, P_{available} \right\} \quad (3.10)$$

Here $P_{available}$ is the power constraint imposed by the electric grid stability, regulations, fuel supply, and the cooling requirements of generators.

Figure 3.5 compares carbon-based materials of varying electrical conductivity, showing the maximum achievable heating rates under laboratory and industrial powers (Eq. 8 combined with $V * I < P_{max}$). Assuming a maximum power input of 2.4 kW for laboratory-scale systems and 1 MW for industrial applications,[139, 140] the graph depicts a peak between graphite and CFP; a higher power is less common or economically non-viable. The graph delineates a power-limited (yellow) and a material-constraint region (orange). In the former, increasing the maximum power

enhances the heating rate. In contrast, the material-constrained regime is bounded by material stability, where a higher power input is infeasible. In this regime, increasing the heating rate requires reducing the heating element's volume. Materials with higher electrical conductivity than carbon fiber paper exhibit lower heating rates due to increased current density (Eq. 3.10), whereas materials with lower electrical conductivity than graphite show reduced heating rates due to power input limitations. This indicates that although materials with low electrical conductivity can theoretically achieve high heating rates, they require significant power input. Consequently, considering the power delivery is essential when selecting Joule-heating materials. Carbon fiber paper is suitable for laboratory-scale applications, while graphite is ideal for pilot-scale. Additionally, higher electrical conductivity correlates with increased thermal conductivity, resulting in isothermal systems and enhanced catalyst utilization, making these materials well-suited for small-scale and industrial applications. The exact value of the maximum power input for laboratory-scale and industrial applications may vary depending on the generator type, system connections, and the geographic region. However, these variations are typically within an order of magnitude and do not alter the material performance trends.

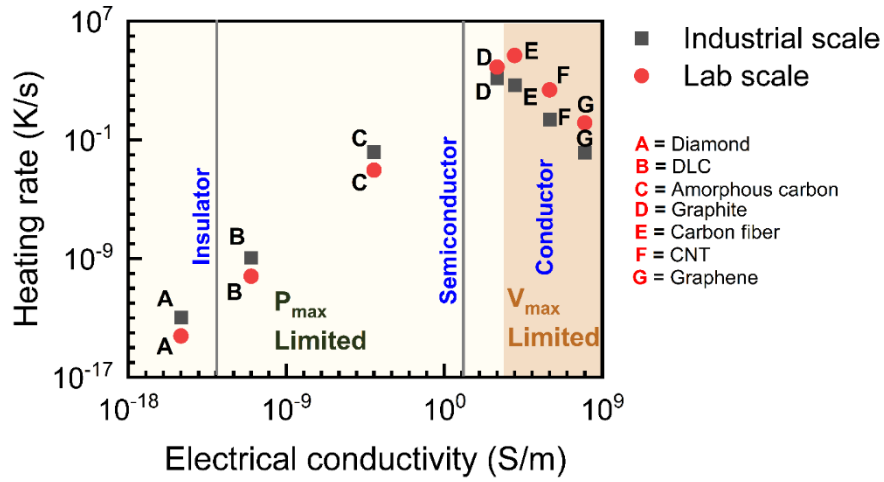


Figure 3.5: Maximum heating rate for carbon materials of increasing electrical conductivity for lab-scale and industrial-scale heating elements. Lab scale maximum power 2.4 kW and a heating element volume of $\sim 0.1 \text{ cm}^3$. Industrial scale maximum power 1 MW and a heating volume 1000 cm^3 .

3.4.3 Optimal Dynamic Operation

The electrical conductivity of carbon-based materials typically increases, while that of metals and alloys decreases, with an increase in temperature. Staying below the current density safety limit requires that the applied voltage must be $\sim 0.8 * V_{max}$ for carbon-based materials, whereas metals and alloys can operate closer to their voltage limit.

Figure 3.6A shows CFD-estimated times to steady state for CFP, SiC, and stainless steel (SS) elements at various starting voltages for two temperatures T_{ss} . SS was chosen to represent both metals and alloys due to its mid-range electrical conductivity. Figure 3.6B shows the CFP temperature trajectory for different initial voltages. A higher voltage significantly reduces the time to steady state by $\sim 10x$ for CFP and SiC (from $0.2 * V_{max}$ to $0.7 * V_{max}$). For stainless steel, $0.2 * V_{max}$ and

$0.5 \times V_{max}$ were insufficient to reach 500 °C, underscoring the need to calculate the minimum required voltage (V_{ss}) for the target temperature. Even at $0.7 \times V_{max}$, the system failed to reach a steady state within 1 s, resulting in a very long response time. The data suggests a strategy to reach steady state faster by applying a voltage above the steady state value and dialing it down to V_{ss} once steady state is reached. For scaled-up elements operating at V_{ss} , the response time scales with $\lambda^{0.25}$, driven by increased mass and reduced cooling rates. In contrast, operating at the maximum heating rate eliminates the dependence on mass or cooling by generating resistive power far exceeding heat losses. This enables millisecond response times even in scaled-up elements, provided sufficient power is available. Leveraging the modular nature of Joule-heated systems, this method reduces industrial downtime and intermittency and allows rapid pulsing for forced dynamic operation.

$$\eta_{startup} (\%) = \frac{\text{Total energy adsorbed}}{\text{Total energy supplied}} \sim \frac{\rho C_p (T_{ss} - T_a)}{(I \times V) t_{ss}} \times 100\% \quad (3.11)$$

The startup energy efficiency ($\eta_{startup}$, Eq. 3.11) is the ratio of the energy accumulated by the heating element to the energy supplied to it. Figure 3.6 shows that starting the system with a higher voltage increases $\eta_{startup}$ to ~ 0.99 when operating at 70% of the voltage safety limit. For stainless steel, the $\eta_{startup}$ remains around 1% owing to the high thermal resistance and long response time. This becomes important for the operation of scaled-up Joule-heated systems. $\eta_{startup}$ also depends on the steady-state temperature; lower temperatures exhibit higher efficiencies due to lower heat losses and shorter transient times. The closer the operation is to the safety limit, the smaller the variation of startup efficiency.

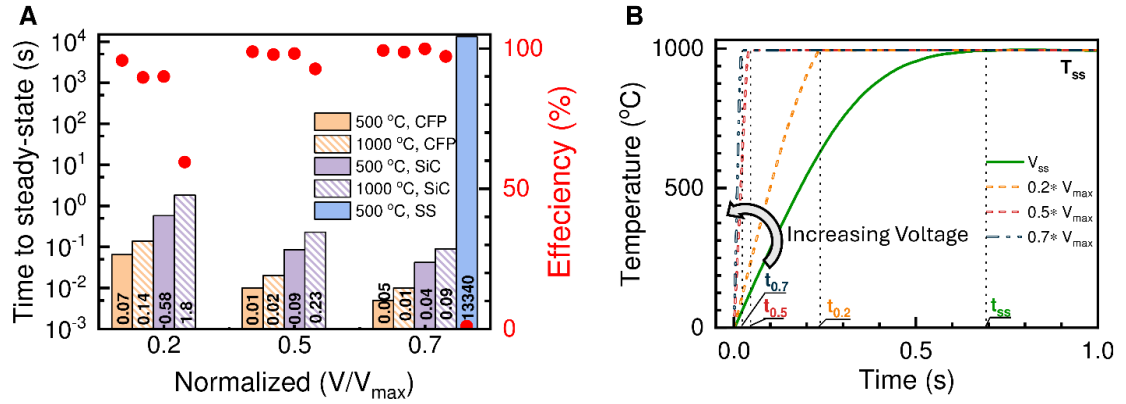


Figure 3.6: Impact of operating voltage on element performance. (A) Time to reach the steady state of 500 °C or 1000 °C and startup energy efficiency for CFP, SiC, and stainless steel (SS) elements. ($V_{max} = 185 \text{ V}$, 215 V , and 0.1 V , respectively; a length of 4 cm and $\lambda = 0.1 \text{ mm}$). Numbers in the bars indicate the time to steady state in s. (B) Effect of initial voltage on the time to reach a $T_{ss} = 1000 \text{ K}$.

3.4.4 Material selection strategy

Figure 3.7 summarizes the workflow for selecting materials to ensure isothermicity, structural integrity, and high startup efficiency. One starts with choosing the target operating temperature (T_{ss}) for process specifications, such as high reaction rates with minimal side reactions, and estimating the element length (L) based on the flow rate for a particular productivity and the required residence time. Selected materials should have a melting point (T_{melt}) above the operational temperature and a thermal conductivity $\kappa > \kappa_{crit}$. If no material satisfies these conditions, the element length and flow rate should be reduced to improve isothermicity. Based on the available power (P_{max}), the maximum voltage should be estimated. If this exceeds the material's voltage limit ($V_{max} = (J_{max} * L)/\sigma$), we should scale down the power (P). If the applied voltage is sufficient to reach the steady-state operating temperature ($V > V_{ss}$), we apply a high voltage for fast heating and reduce the voltage to V_{ss} upon

reaching the steady state. Otherwise, the element length could be reduced or the volume-to-surface area ratio increased, and the procedure repeated.

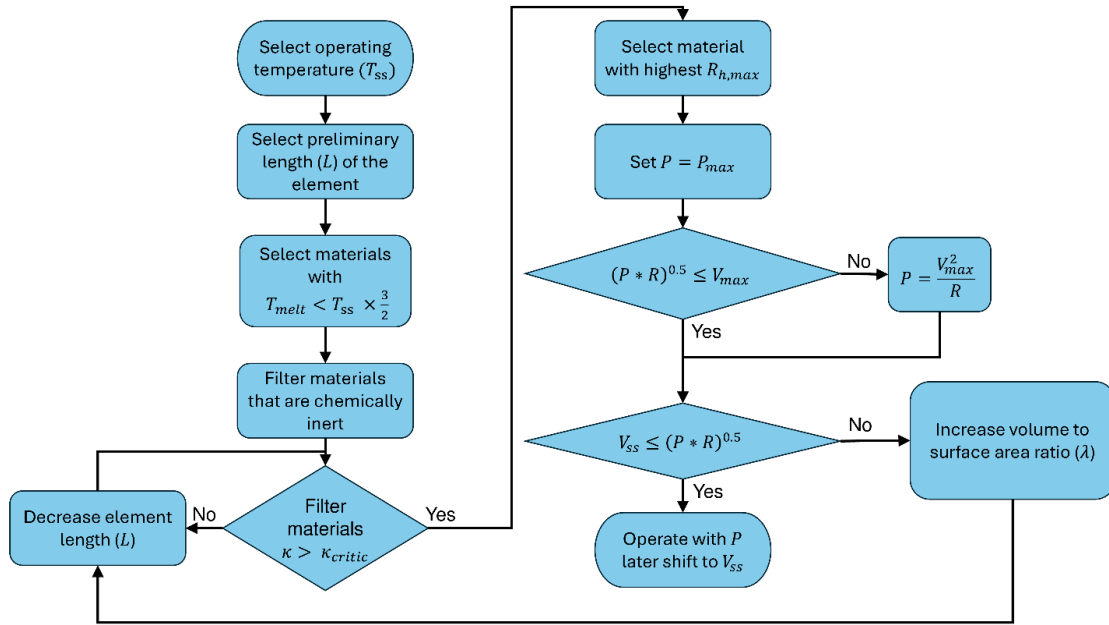


Figure 3.7: Flow diagram outlining the material selection and design process for Joule-heated systems, ensuring isothermicity, structural integrity, and high startup efficiency. R is the total resistance of the element.

3.4.5 Impact of heating element's porous structure

Heating elements may possess random or engineered (3D printed) porosity and tortuosity (the ratio of the actual to the minimum conduction path) to achieve a high surface area for catalysis. Here, we consider porous heating elements with punctured tubular pores along the length (Figure 3.8A), the width (Figure 3.8B), or uniformly distributed (Figure 3.8C). We investigate copper, stainless steel, and carbon fiber paper that cover a broad spectrum of electrical and thermal conductivities.

Figures 3.8A–C show that the CFD-predicted current density in CFP heating tapes varies spatially in a profound way. High current density spots form near the pores, along the direction of current flow, whereas low current density spots form between pores that obstruct electron flow. Despite identical porosity (Figures 3.8A and 3.8B), the structure affects the maximum current densities and their corresponding locations. In structured systems like foams, branching networks would reduce the effective cross-section (constriction), while nodes before branch points (as shown in Figure 3.8A) would concentrate the current, potentially reaching current safety limits with localized overheating and failure via electromigration. Overall, higher tortuosity and smaller constriction factors reduce the average current density due to longer paths and narrower channels for the flow of current. Monolithic structures, with uniform cross-sections, offer a potential solution to mitigate these limitations. Figures 3.8D and E quantify the effects of porosity on the steady-state volume-averaged current density, temperature, and their variation (CV). Higher porosity lowers the average current and temperature, causing significant current non-uniformity. Due to the high conductivity of the CFP, temperature hot spots are minimal. Similar trends are observed for stainless steel and copper (Section B.8), but stainless steel exhibits temperature inhomogeneity (see also next).

As the system's complexity increases, detailed CFD simulations become computationally expensive. To reduce computational cost, we employ coarse-graining, considering a single unit cell whose periodic translation can fill the space (homogenization theory).[132] Here, a tubular pore of varying diameter was introduced, limiting porosity to 70% to maintain structural integrity, for illustrative purposes. Given the separation of length scales, the pore shape has minimal influence

on the results. As the porosity increases, σ_{eff} varies slightly, consistent with Figure 3.8D, which showed minimal changes in the average current density (more details in Section B.9). In contrast, the effective thermal conductivity (Eq. B.16) decreases (see typical results in Figure B.10 for symmetric and asymmetric pores).

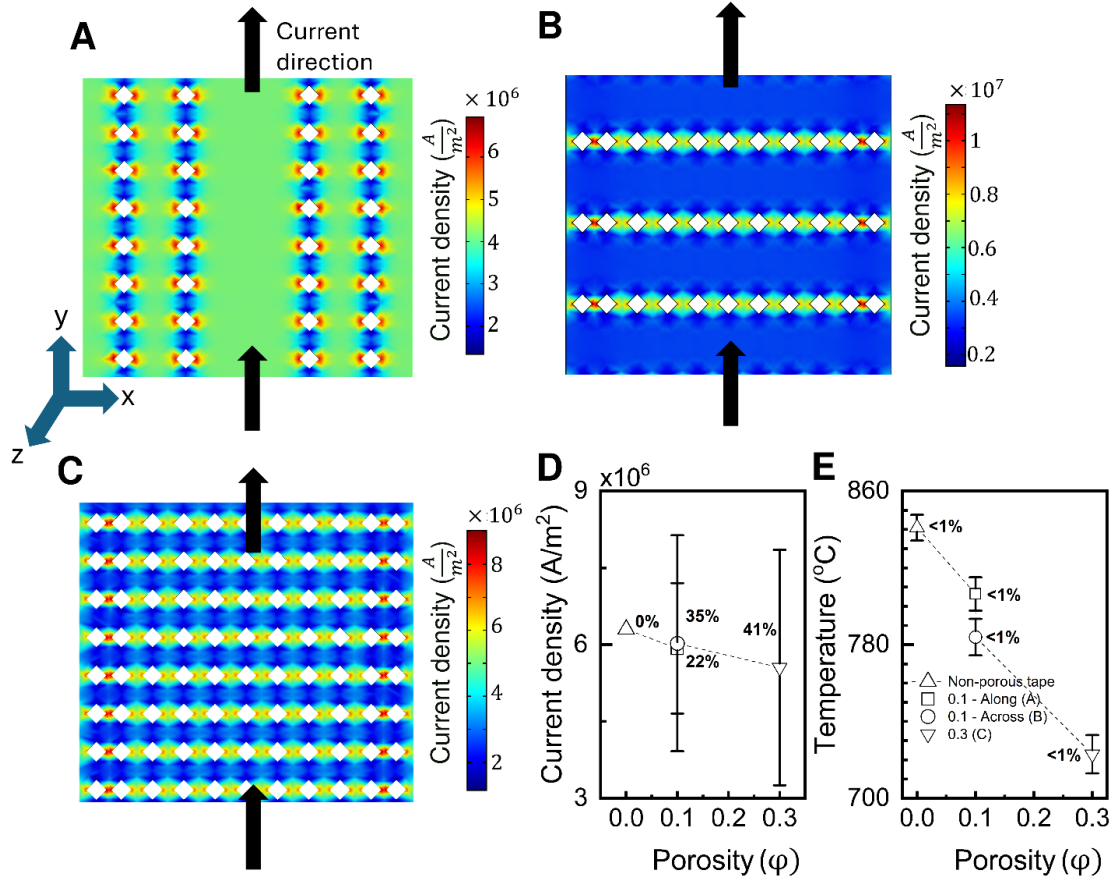


Figure 3.8: Side-view of the current density in CFP heating tapes with (A) 0.1 porosity along the length, (B) 0.1 porosity along the width, and (C) 0.3 porosity with uniform pore distribution. The color bar scale is similar but not the same to highlight the ‘hot’ spots of high current density. Porosity-specific volume-averaged current density (D) and temperature (E) for CFP at 15 V. The numbers represent the CV, and the bars indicate the variance across the volume.

Figure 3.9A presents side views of CFD-computed current density distributions in unit cells with varying porosity. The current density peaks near the pore edges in the direction of electron flow, consistent with Figures 3.8A–C. Figure 3.9B displays the temperature field for materials with varying thermal conductivities. Significant temperature gradients are observed for materials with low thermal conductivity, such as FeCrAl. Materials with modest thermal conductivity, such as stainless steel, exhibit some temperature gradients concentrated around the pores, and materials with high thermal conductivity, like CFP and copper, are essentially isothermal.

Figure 3.9C shows the volume-averaged resistive power density over a non-porous heating tape ($\frac{\langle Q_{eh} \rangle_\phi}{\langle Q_{eh} \rangle_{\phi=0}}$). It scales as $1 + \alpha$, where α is the increase in the current density with increasing porosity stemming from the larger electrical resistance caused by the reduced cross-sectional area ($R = \frac{L}{\sigma * A}$). The same voltage leads to an increased resistive power density ($Q_{eh} = I * V$) as the porosity increases. The heating rate $R_h = \frac{\langle Q_{eh} \rangle_\phi}{\rho C_p} = \frac{\langle Q_{eh} \rangle_{\phi=0} * (1 + \alpha)}{\rho C_p} = \frac{\sigma V^2 (1 + \alpha)}{\rho C_p L^2}$ increases with increasing porosity for any given geometry. Foams and porous structures of high porosity are especially prone to both elevated resistive power density hotspots and risks of electron migration, and potential temperature gradients. Point measurements are necessary to accurately characterize the temperature distribution within a system.

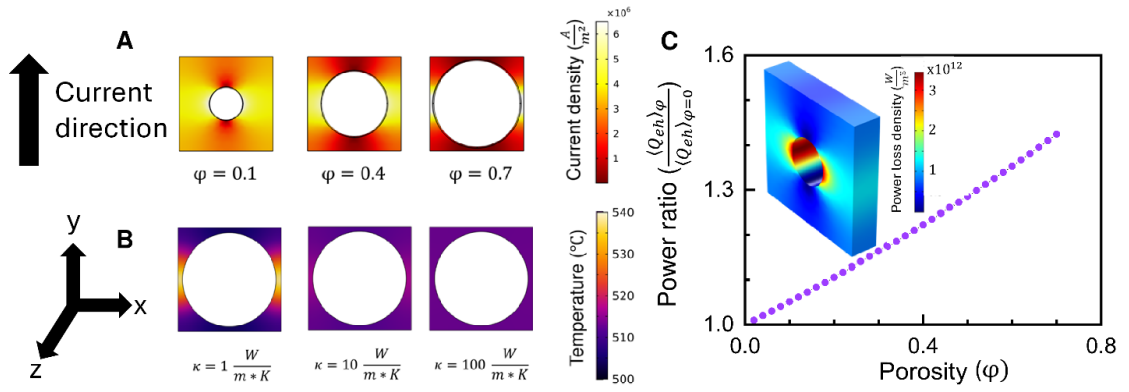


Figure 3.9: Effect of porosity on the current, temperature, and power dissipation. Side view of the (A) current density with varying porosity of CFP tapes, and (B) temperature for materials with varying thermal conductivity for 0.7 porosity. (C) Power enhancement due to porosity for a CFP tape. The inset shows the power loss density map for a porosity of 0.4.

3.5 Conclusion

This study evaluated materials for Joule heating, highlighting key factors that influence performance, scalability, and stability. Carbon-based materials, particularly carbon fiber paper (CFP) and graphite, emerge as the most suitable choices due to their high heating rates, rapid response times, and efficient power utilization. Their ability to achieve millisecond-scale response times and near-unity startup efficiency makes them ideal for dynamic and pulsed heating applications, thereby mitigating intermittent energy issues. Material properties fundamentally dictate system performance. The electrical conductivity and volumetric heat capacity control the maximum heating rate. The volume-to-surface area ratio and heating element structure significantly affect the steady-state temperature and power consumption. Thermal conductivity and heating element structure govern temperature isothermicity. Structure engineering, such as introducing porosity, enhances heat and mass transfer but necessitates careful optimization to prevent excessive current localization, which can

lead to material failure due to electromigration and thermal runaway. The findings indicate that monolithic structures may offer a balance between thermal efficiency and mechanical stability, particularly in large-scale applications. Furthermore, this work highlights the significance of startup conditions in system design. Overall, this study establishes a framework for optimizing Joule-heated system design by integrating material properties, electrical and thermal considerations, and structural geometry.

Chapter 4

SHORT CONTACT TIME, HIGH TEMPERATURE, INTERNALLY-HEATED ETHANE CRACKERS

4.1 Contributions

This chapter contains published work,[8] performed for this thesis. Yeonsu Kwak performed all experiments. The rest of the work was performed by this thesis' author.

4.2 Introduction

Ethylene (C_2H_4) is a platform chemical used in the production of plastics, fibers, and other chemicals. Its production volume (>200 million metric tons annually)[16, 141, 142] is the largest among organic chemicals. The conventional production process of thermal steam cracking of naphtha or ethane (C_2H_6)[9] uses a lot of energy to heat the endothermic reaction, producing substantial carbon dioxide (CO_2) emissions due to fuel combustion[143] and volatile organic compound (VOC) emissions.[144] Steam cracking operates at a residence time (τ) of $\tau \sim 0.1$ s, with (33 mol%) steam dilution, and rapid quenching (0.02-0.1 s) to mitigate radical-initiated coking.[145, 146] Temperature critically dictates yields; higher temperatures favor C_2H_4 , C_6+ , CH_4 , and coke byproducts.[11, 23, 108] To avoid exotic, expensive reactor wall materials, the typical temperature is $850^\circ C$ (a tube temperature ceiling of $<1000^\circ C$), leading to 53% C_2H_4 yield and 79% selectivity at $750\text{--}900^\circ C$. The process

exhibits energy losses and temperature gradients ($>100\text{ }^{\circ}\text{C}$) that promote coke in high-temperature regions.[147]

Electrified steam crackers are emerging as cleaner alternatives, employing either direct resistive heating, in which an electric current passes through the cracking coils, or indirect resistive heating, in which external elements radiatively transfer heat to the coils. Both approaches are designed to reach $800\text{--}900\text{ }^{\circ}\text{C}$ under pressures typical of industrial steam cracking.[18, 148, 149] Developing intensified heating to achieve uniform, internal gas temperatures of $>1,000\text{ }^{\circ}\text{C}$ could optimize C_2H_4 yield, bypassing heat transfer resistances through the walls and minimizing energy losses and byproduct formation, leading to innovative manufacturing.

This study investigates *internally Joule-heated C_2H_6 crackers* to heat the gases directly, bypassing external energy transfer and wall material limitations.[76, 150] This catalyst-free electrification strategy can achieve uniform and high temperatures ($>1000\text{ }^{\circ}\text{C}$) and short contact times ($<10\text{ ms}$) to quench secondary reactions and maximize C_2H_4 yield. This study employs a multi-faceted approach using modeling to explore the unknown operational window and then validating these predictions through targeted experiments. First, we used a lumped kinetic model (LKM) to map the optimal window that maximizes ethylene while minimizing methane and aromatics. This window was found to be outside the original development regime of the LKM, raising questions about its extrapolation accuracy. We then validated this window and elucidated pathways with a comprehensive gas-phase microkinetic model (MKM). To translate these targets to our non-ideal, non-isothermal carbon-fiber-paper (CFP) based Joule-heated reactor, we coupled an adjusted LKM with computational fluid dynamics (CFD). The LKM–CFD framework specified experimental conditions

to maximize $Y_{C_2H_4}$ for targeted experiments. We benchmark performance metrics (yield, selectivity, conversion) against industry standards, and conduct techno-economic analysis and life-cycle assessment. Ultimately, this study provides insights into next-generation electrified reactors for intensified, selective, and decarbonized olefin production.

4.3 Methods

4.3.1 Kinetic models

All equilibrium composition data was calculated using the Thermosolver.[151] Coke is represented as solid carbon (C(S)), which has properties similar to graphite. Two kinetic models are utilized for this work: a lumped kinetic model and a detailed microkinetic model. The lumped kinetic model (Section C.1), previously reported by *Ranjan et al.*, [152] comprises 11 reactions and 11 molecular species. This model and its revision were implemented in a PFR and a three-dimensional (3D) CFD model and solved using COMSOL.[115]

The microkinetic model, adopted from previous publications,[153, 154] was converted into OpenMKM format.[155] OpenMKM features state-of-the-art C++ solvers and is compatible with RenView[156] for Reactor Pathway Analysis (RPA). This detailed model comprises 501 chemical species and 9,286 reactions, including CH_4 non-oxidative coupling and C_3H_6 pyrolysis reactions. Simulations using this model were performed in an isothermal and isochoric PFR.

4.3.2 CFD

We simulate a Joule-heated system comprising of an elongated CFP connected to two centrally located copper electrodes inside a cylindrical tube, with gas flowing

parallel to the CFP's length. The model accounts for energy transport in the heating element, chemical reactions, flow, species transport, and energy conservation in the surrounding fluid. Heat transfer between the solid and fluid phases are rigorously captured, including all interface effects. The energy equation, reaction kinetics, concentrated species transport, continuity equation for compressible fluids, and Navier–Stokes equations are solved using the COMSOL Multiphysics package.[115] The equations were solved using the built-in finite element solvers (Section C.1).

4.3.3 TEA/LCA

A techno-economic model was developed to estimate the total capital investment and manufacturing costs for C_2H_4 production via C_2H_6 steam cracking, based on the following assumptions: a tax rate of 35%, an inflation rate of 3%, 20-year depreciation, a revenue interest rate of 15%, a debt interest rate of 5%, and an annual operating period of 8000 h. A capital charge factor (CCF) of 0.1 was assumed, consistent with these financial parameters.[62] The TEA was conducted using the Aspen Process Economic Analyzer V12. Heat integration was performed using the Aspen Energy Analyzer V12. Details are provided in Section C.2. LCA was used to compare conventional with Joule-heated C_2H_6 cracking. A “cradle-to-gate” system boundary was adopted, encompassing raw material extraction, utility generation, and production stages. For each production route, the unit-specific inventory is detailed in Section C.3. Data were sourced from Ecoinvent 3.9[157] and evaluated using the ReCiPe 2016 method.[158]

4.3.4 Reactor Setup

C_2H_6 thermal cracking experiments were conducted using a custom-designed Joule-heated reactor system. The core of the reactor consisted of a vertically oriented quartz tube (17 mm inner diameter, 19 mm outer diameter). The heating element was a Freudenberg H23 carbon fiber paper (CFP) with a thickness of 0.21 mm with 95 g/m². The CFP, cut to a typical length of 10 mm and a width of 38 mm $\times$ 8 mm, was positioned in the center of the quartz reactor. Additional element sizes were also employed. For electrical connection and mounting, the CFP was clamped at its edges by flat copper plates, which were in turn connected to stainless steel clips. These clips, with electrical connections at the top, provided the current path for Joule heating. This arrangement ensured the CFP was suspended in the middle of the reactor, allowing for uniform gas flow around the heating element. The reactor design enables extremely steep thermal gradients, as demonstrated by the axial temperature profile. The heating zone is highly localized around the CFP element, with temperatures rising sharply from ambient ($\sim 20^\circ\text{C}$) to the target reaction temperature (typically 1000°C) over a distance of less than 5 mm. This creates an exceptionally steep temperature gradient of approximately $-200^\circ\text{C}/\text{mm}$ in the cooling zone downstream of the heating element, enabling rapid quenching of reaction products and minimizing secondary reactions. The system was operated without external thermal insulation, allowing direct visual observation of the heating element through the transparent quartz reactor wall. This open-air configuration also contributed to the rapid cooling during pulsing, with heat dissipating via convection and radiation. Precise gas flow control was maintained throughout the experiments.

4.3.5 Temperature Measurement

Temperature measurements of the CFP were acquired using an IR camera (PI 1M, Optris) with a detection range of 450-1800 °C, positioned to view the CFP through the quartz tube. Due to limitations in accurate IR detection at lower temperatures (<450 °C) encountered during the cooling phase of RPH cycles, a mathematical correction approach was implemented. The cooling rate was approximated with a power law relationship ($dT/dt = a \cdot T^b$ (K/s)), where $a = 3.26 \times 10^{-6}$ and $b = 2.88$ were determined by fitting experimental data at higher temperatures. This relationship was then extrapolated to lower temperatures. Periodic cycles oscillated between a peak temperature (T_{peak}) and a minimum temperature (T_{min}) with a time-averaged temperature (T_{avg}).

4.3.6 C₂H₆ Cracking Experiments

Power input to the CFP was managed by a DC power supply (HY7520ex, 75V, 20A, 1500W). This supply was coupled with a programmable heating system consisting of an arbitrary function generator (AFG1062) connected to a DC solid-state relay (ZGT-25DD) to modulate the power. Two heating modes were investigated: power pulses at a frequency of 1 Hz, consisting of a 50 ms heating period followed by a 950 ms cooling period (representing a 5% heat duty cycle), and CJH with a constant power input to maintain a steady-state temperature. For C₂H₆ cracking, a flow of 5 mol% C₂H₆ in high-purity helium (99.999%) was introduced at a total flow rate of 50 SCCM. The gas mixture was directed downward through a vertical reactor. All reactions were allowed to reach a steady state, typically over a period of 10 min, before product sampling. Product analysis was conducted using a micro-GC (MicroGC 990, Agilent) and a standard GC (7890B, GC/FID, HP-PLOT Q, 30 m ×

530 $\mu\text{m} \times 40 \mu\text{m}$, Agilent,)), with helium serving as an internal standard to account for volume changes during the reaction. Repeat errors were below 1-2%. Carbon balance was determined using GC-FID, which provides a signal proportional to the number of carbon atoms in a molecule. Calibration with a standard gas mixture (VGM-3 and VGM-10, Mesa gas) was used to determine relative response factors, calculated by comparing the FID signal of each species to a reference. The RRFs showed a linear relationship with carbon number, enabling estimation of product concentrations without available standards. For species with standards, direct calibration was performed.

4.4 Results and discussion

4.4.1 Thermodynamics, Reaction Network, and Reaction Pathway Analysis

Equilibrium calculations were first used to identify dominant species in C_2H_6 cracking at 1 atm and 500–1500 °C (Figure 4.1a). Above 600 °C, solid carbon ($\text{C}(\text{S})$), hydrogen (H_2), and, to some extent, CH_4 dominate, whereas C_2H_6 , C_2H_4 , and acetylene (C_2H_2) are rather minor. Benzene (C_6H_6) and other aromatics are present at concentrations below 1 ppm but increase with temperature. The inset in Figure 4.1a shows that below 800 °C, C_2H_6 is the dominant C_2 species and C_2H_4 is the primary C_2 product. At moderate temperatures (800–1150 °C), C_2H_4 is the dominant C_2 species and at >1150 °C, C_2H_2 is the dominant C_2 species. Figure C.1 shows equilibrium calculations with H_2O included in the feed and CO and CO_2 in equilibrium product yields. It shows that at high temperatures, H_2O reacts with $\text{C}(\text{s})$ to form CO and CO_2 .

A lumped kinetic model (Section C.1)[152, 159] was used to study the reaction pathways. The reaction network (Figure 4.1b) is based on lab-scale[160, 161] and

industrial data[12] reported in the literature for temperatures between 800-900 °C and a residence time ~100 ms. The network identifies $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ (Pathway 1) as the preferred route to produce C_2H_4 , with minor C_2H_4 production via C_3H_6 (Pathway 2).[159] Competing pathways include C_2H_6 hydrogenolysis to CH_4 and C-C coupling to C_3H_8 formation (Pathway 3).[159] C_2H_4 is also consumed to C_6H_6 and C_4 .

Levenspiel plots (Figure 4.1c, across 900–1400 °C) show that increasing temperature accelerates reaction rates, particularly at low conversions, as evident from the leftward shift of the curves. However, the rate drops sharply due to reverse reactions at higher conversions, especially near equilibrium. Feed dilution lowers the initial C_2H_6 consumption (Figure 4.1d) but delays the rate suppression, enabling higher overall conversions. Levenspiel plots also allow comparison of reactor volume requirements to attain the same conversion in a Plug Flow Reactor (PFR) and a Continuous Stirred Tank Reactor (CSTR). For PFRs, the required volume is the area under the curve, while for CSTRs, it is the product of the ordinate and abscissa at a given conversion. Figure 4.1c–d suggests that PFRs are significantly smaller. Therefore, a PFR was selected for subsequent high-temperature reactor studies.

The lumped kinetic model was first validated against experimental data at 835 °C (Figure 4.1e). The results match the experimental product composition closely, confirming the model's accuracy at <900 °C and longer residence times where the model was developed. PFR-based residence time data at 900 °C (Figure 4.1f) shows high C_2H_6 conversion to C_2H_4 up to 0.05 s; longer residence times increase unwanted secondary products (CH_4 and aromatics). Overall, the kinetic calculations indicate a process far from the equilibrium composition shown in Figure 4.1a.

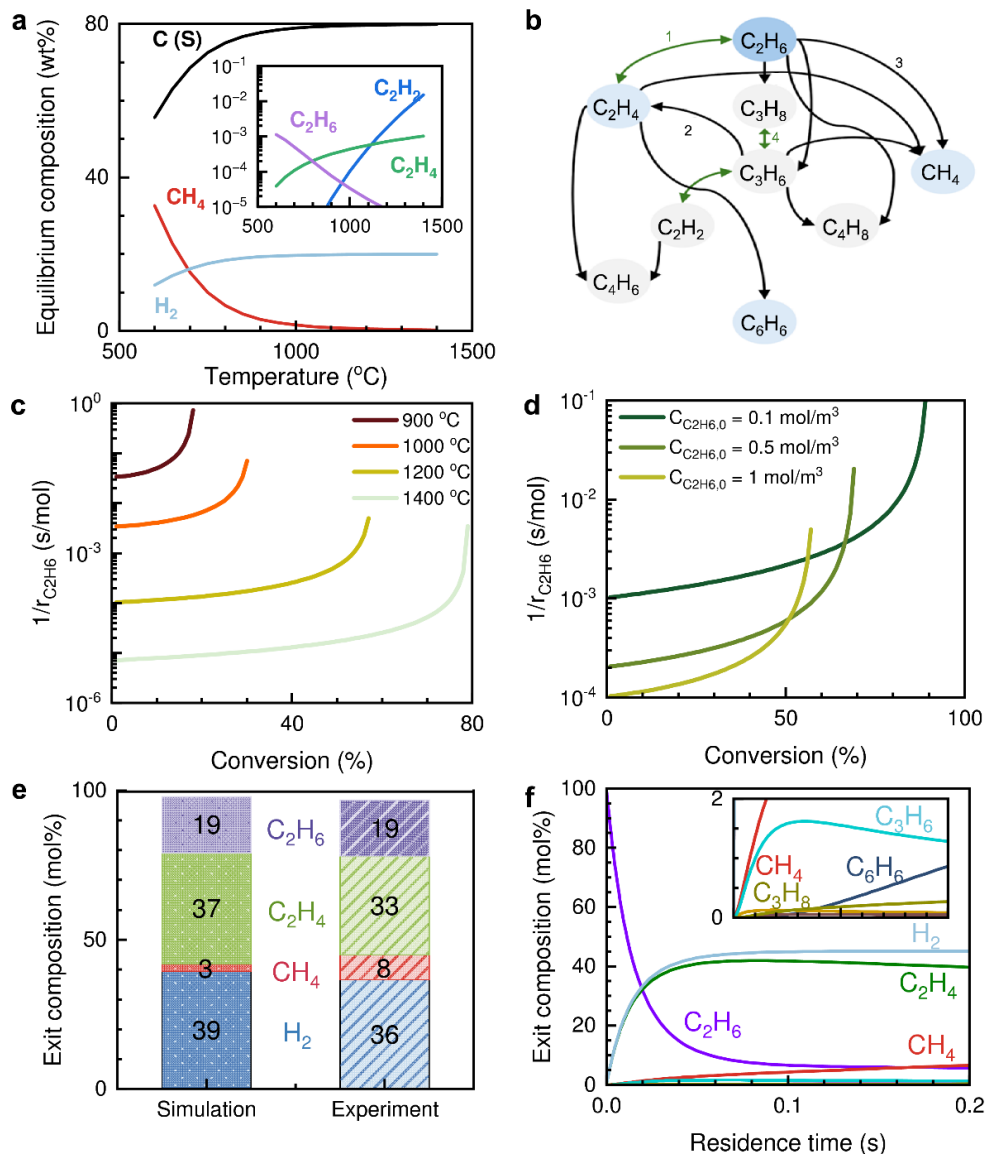


Figure 4.1: C_2H_6 thermal cracking model calculations. (a) Equilibrium species composition as a function of temperature at 1 atm, with 100% of C_2H_6 fed as a reactant; inset: magnification of C_2 species. Only species with $wt\% > 10^{-5}$ are shown. Non-coke calculations are shown in Figure C.1. To reach equilibrium, the contact time in the reactor should be longer than the other governing time scales. A detailed discussion of all time scales was provided by Balakotaiah et al.[23, 24] (b) Lumped reaction network based on lab-scale and industrial data for temperatures between 800-900 °C and a residence time ~ 100 ms. Dark blue represents the reactant, light blue indicates major products, and grey denotes minor products. Green (black) edges indicate equilibrium (forward) reactions. (c) Levenspiel plot at 900–1400 °C, 1 atm, with an inlet concentration $[C_2H_6]$ of 1 mol/m³. (d) The Levenspiel plot with varying inlet $[C_2H_6]$ at 1000 °C and 1 atm. (e) Experimental[162, 163] vs. simulated exit composition at 835 °C, 1.9 atm, 0.4 kg_{steam}/kg_{C₂H₆}, and $\tau = 0.2$ s. (f) Exit composition vs. residence time at 900 °C and 1 atm in a PFR with 0.3 kg_{steam}/kg_{C₂H₆}. Data reported on a dry basis for e and f.

4.4.2 Optimal Operating Conditions

Maximizing C_2H_4 yield reduces the downstream separation load and improves economics. Minimizing C_6H_6 production can reduce coke and extend run time. Finally, minimizing CH_4 in electrified crackers is important because CH_4 will not be needed as heating fuel. PFR simulations using the lumped kinetic model were conducted to map the thermal cracker performance at 1 atm, 0.3 kg_{steam}/kg_{C₂H₆}, 800–1400 °C, 0–100 ms (Figure 4.2). The C_2H_6 conversion ($X_{C_2H_6}$) exceeds 90% at temperatures > 1000 °C with $\tau > 10$ ms (Figure 4.2a). The C_2H_4 yield ($Y_{C_2H_4}$) is sensitive to reactor temperature: it peaks at 80–85% above 1000 °C and $\tau < 10$ ms (Figure 4.2b). Longer residence times at high temperatures promote secondary reactions to CH_4 and C_6H_6 /coke (Figure 4.2c-d). Intermediate residence times (10–60 ms) result in moderate C_2H_4 yields due to secondary reactions. Finally, lower temperatures and longer residence times, typical of the industrial baseline operation,

lead to lower C_2H_6 conversion and ethylene yield. The optimal yield of ~ 85 wt% is significantly higher than that of ~ 53 wt% at industrial conditions.

The results underscore high temperatures with ultra-short residence times (1000–1150 °C, <10 ms) maximize $Y_{\text{C}_2\text{H}_4}$ and retard CH_4 and aromatic byproduct formation. Temperature gradients will lower the C_2H_4 yield (Figure 4.2b) and lead to coking in high-temperature near-wall regions needed to have a hot interior (Figure 4.2d). Due to wall material limitations, such temperatures cannot be achieved with external heating. We propose that internal heating can reach high temperatures without reactor tubing stability challenges. The lumped kinetic model was developed below 900 °C and longer than optimal residence times, so validation of predictions at near-optimal conditions is required given the optimal yield is significantly higher than the industrial one.

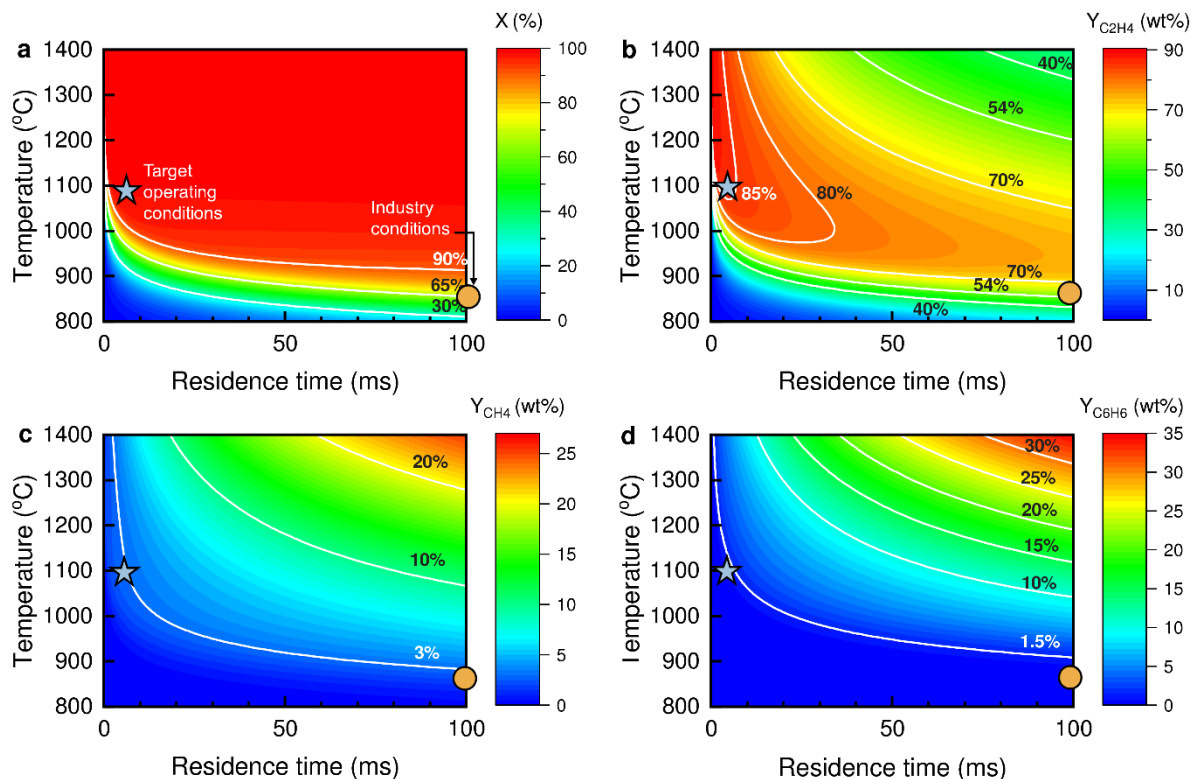


Figure 4.2: Predicted (PFR) reactor performance maps (dry basis data, Feed: 70 mol% C_2H_6 and 30 mol% H_2O and 1 atm) using the lumped kinetic model. (a) Ethane conversion ($X_{C_2H_6}$), (b) ethylene yield ($Y_{C_2H_4}$), (c) methane yield (Y_{CH_4}), and (d) benzene yield ($Y_{C_6H_6}$). Yellow circles: industrial conditions ($T \sim 800\text{--}900^\circ\text{C}$ and $\tau \sim 0.1$ s). Blue stars: target conditions ($T \sim 1000\text{--}1500^\circ\text{C}$ and $\tau \sim 5\text{--}10$ ms). The solid lines represent iso-contours. The white numbers represent the iso-contour corresponding to industrial performance.

To extend mechanistic understanding and assess the lumped model's results, a comprehensive MKM was employed.[153] Unlike lumped models, MKM includes elementary reaction steps, potentially missed by lumped models. Due to higher computational cost, the MKM was used within a narrower, near-optimal operating window ($1000\text{--}1200^\circ\text{C}$, $\tau < 20$ ms) using a 70 mol% C_2H_6 and 30% He mixture at 1 atm (Figure 4.3). The results show strong temperature sensitivity: $X_{C_2H_6}$ exceeds

85% at 1150 °C with $\tau < 5$ ms, whereas a similar conversion at 1050 °C needs a longer residence time of $\tau > 15$ ms (Figure 4.3a). The $Y_{C_2H_4}$ peaks at > 65 wt% at 1000–1200 °C with $\tau \sim 2$ –10 ms (Figure 4.3b). The optimal residence time for maximum yield decreases with increasing temperature, defining a narrow window of ~ 5 ms residence time and a temperature within ± 25 °C. CH_4 formation increases above 1050 °C, reaching 3 wt%, doubling by 1100 °C, and tripling by 1200 °C, establishing an upper temperature (Figure 4.3c). C_6H_6 formation increases above 1120 °C, reaching 5 wt%, doubling by 1200 °C (Figure 4.3d). A 2 orders-of-magnitude difference is observed in the predicted $Y_{C_2H_2}$; the lumped model predicts ~ 0.1 wt% compared to ~ 10 wt% of the MKM (Figure C.2). Deviations are also observed for aromatic yields. Key differences between the MKM and lumped models include the significantly lower optimal ethylene yield (65% vs. 85%) and higher byproduct yields (methane, acetylene, and benzene) of the former.

Reaction pathway analysis under conventional conditions (900 °C, 0.1 s; Figure 4.3e) reveals that C_2H_6 primarily forms ethyl radicals through hydrogen abstraction by hydrogen radicals (82% of the flux) and methyl radicals (18% of the flux), with 86% of the ethyl radicals converting to C_2H_4 . Minor pathways lead to methyl, vinyl, and C_3 species. At target conditions of 1100 °C, 2 ms (Figure 4.3e), the ethyl-to- C_2H_4 selectivity reaches 95% with minor direct C-C bond scission to CH_3 . Even at short residence times, secondary C_2H_4 transformations lead to vinyl radical (43%), which further undergoes C_2 coupling and H abstraction. While vinyl directly dehydrogenates to acetylene (C_2H_2) at high temperatures, it is aided by C_2H_4 at industrial conditions, shifting C_2H_2 formation from bimolecular (at industrial conditions) to unimolecular (at high temperatures). Figure 4.3e and Figure 4.3f also

show that while the lumped kinetic model captures major pathways, it omits direct dehydrogenation via H removal of C_2H_4 to C_2H_2 , which becomes important at high temperatures, where C_2H_4 also participates in CH_4 formation. This omission explains the difference in predicted yields of the lumped model (Figure 4.2b-c) and the detailed microkinetic model (Figure 4.3b-c).

Like the lumped kinetic model, the MKM results indicate that uniform, higher temperatures and shorter residence times than industrial systems effectively convert C_2H_6 to C_2H_4 and quench secondary reactions, such as aromatization via C_4 intermediates. Given the lumped kinetic model validation was done at lower temperatures and the MKM model was developed for pyrolysis and combustion (higher) temperatures, we assess model predictions below with experiments and associated CFD simulations.

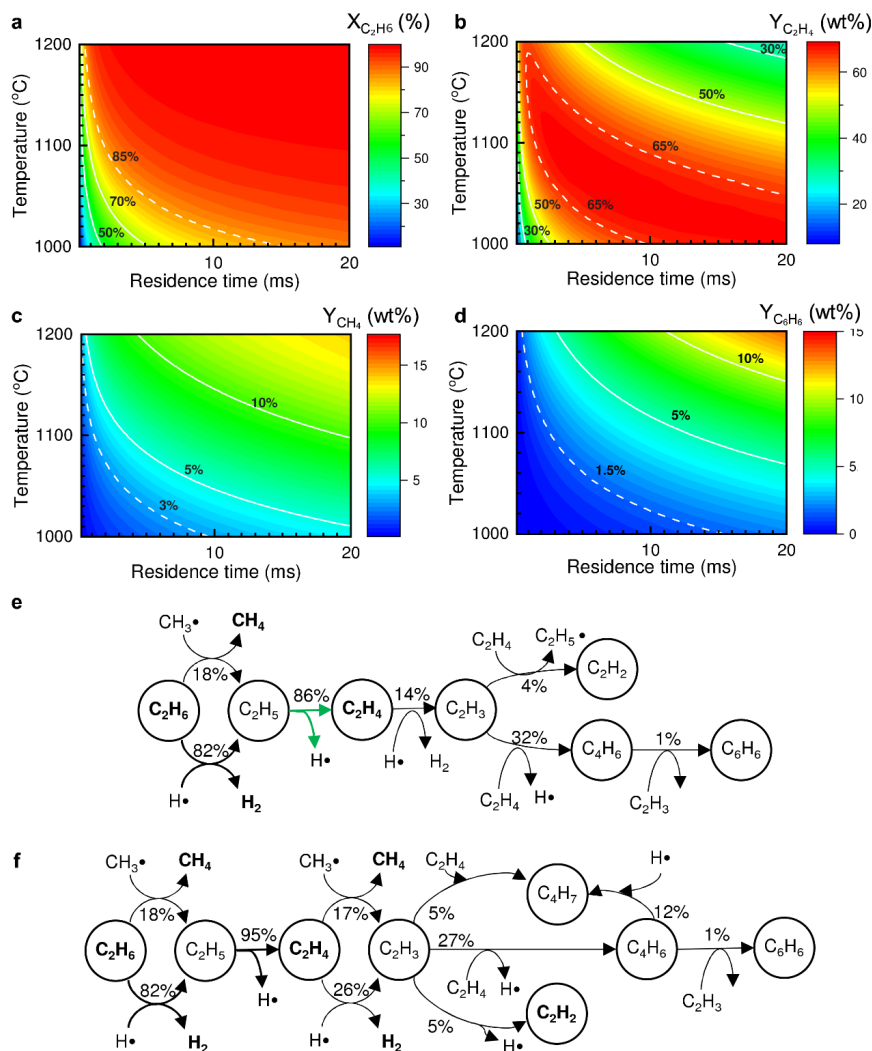


Figure 4.3: Predicted (PFR) reactor performance using the microkinetic model (MKM) on a dry basis. Feed: 70 mol% C_2H_6 and 30 mol% He and 1 atm. (a) $X_{C_2H_6}$, (b) $Y_{C_2H_4}$, (c) Y_{CH_4} , (d) $Y_{C_6H_6}$. Solid lines represent contours, and dashed lines target operating boundaries. (e) Reaction pathway analysis at conventional conditions (900 °C, 0.1 s): high ethyl radical flux with limited secondary reactions. (f) Pathway analysis at target conditions (1100 °C, 2 ms): enhanced SC_{2H_4} with suppressed methyl and C_2H_4 coupling to C_{4+} . Node labels represent a species (bold labels represent dominant species). Green edges represent partially equilibrated reactions; black edges indicate non-equilibrated reactions. Edge thickness reflects reaction rates normalized to the initial reactant flow. Percentages indicate molar selectivity relative to the initial reactant; values may not equal 100% due to rounding or omission of minor pathways. Uncertainty analysis results shown in Figure C.13.

4.4.3 CFD Simulations and Experiments

While the ideal kinetic models identified an optimal operational window, we next assessed these theoretical predictions through targeted experiments and computational fluid dynamics (CFD) to account for non-ideal reactor conditions. While the optimal yield is kinetic-model dependent, the optimal operating conditions of higher temperatures of 1000-1150 °C and shorter residence times of <10 ms are insensitive to model details. Although integrating CFD with the microkinetic model (MKM) could be more insightful, it would also significantly increase computational cost. Since the objective of this study was to identify approximate operating conditions that maximize $Y_{C_2H_4}$ while minimizing Y_{CH_4} and $Y_{C_6H_6}$ in the experimental reactor, the use of CFD coupled with a LKM was suitable for our purposes. With this finding, we conducted Joule-heated experiments to assess model predictions. CFP was selected over other materials due to its high maximum heating rates and near-unity startup efficiency.[7] Alternative internal heating elements, such as wires and cylindrical rods, offer greater structural stability but are prone to significant thermal gradients. The high thermal conductivity of the CFP results in high temperature uniformity with cold edges (more pronounced experimentally due to the copper clip contact), as confirmed using an infrared (IR) camera and CFD simulations (Figure 4.4ai&ii). The direct heating and high temperature resilience of the CFP allow high internal (heating element and gas) temperatures (up to ~2000 °C), bypassing heat transfer resistances while maintaining cold walls (Figure 4.4aiii). This eliminates temperature restrictions imposed by the material of the reactor tube walls. The current CFP reactor achieves high temperatures in a tiny ‘reactive volume’ of hot fluid confined near and inside the CFP (a 70% porous structure of ~210 μm thickness), where chemistry happens (Figure 4.4aiii). Radiative and convective heat losses quench the gas rapidly outside this small

volume; the rest of the fluid is cold.[117] A lower bound of the contact time (τ) is $\sim \frac{V_{element}}{\dot{Q} \cdot \theta}$, where $V_{element}$ is the heating element volume, $\dot{Q}$ is the inlet flow rate, and θ relates to the volume expansion due to the increased temperature. For a CFP of $1 \text{ cm} \times 0.8 \text{ cm} \times 0.021 \text{ cm}$ at 300 sccm and 1100 °C, $\tau \sim 0.74 \text{ ms}$. A reactive zone of $\sim 1 \text{ mm}$ on each side of the CFP gives a residence time of $\sim 14.5 \text{ ms}$. These estimates indicate that the CFP reactor can achieve high temperatures and short residence times, but the latter is longer than desired. We elaborate further on this point below.

Experimental data at various residence times (by varying the flow rate and heating CFP length (L)) and temperatures are shown in Figure 4.4b. As the temperature increases, the C_2H_6 conversion and the C_2H_4 and CH_4 mole fractions increase (Figure 4.4b). The CFD, with the lumped kinetic scheme, predicts selectivities in agreement with experimental data at the same conversion, but overpredicts $X_{\text{C}_2\text{H}_6}$ (Figure C.3) due to the extrapolation of the lumped kinetic model (some errors also occur due to temperature reduction near the Cu contacts). Therefore, the activation energy of the C_2H_6 dehydrogenation step was adjusted from 272.8 kJ/mol[152] to 292.8 kJ/mol. This step was chosen due to its rate-determining nature. The final value was obtained by gradually increasing the activation energy until a desired mean-square error was achieved (root mean square error, $\text{RMSE}(X_{\text{C}_2\text{H}_6}) < 0.05$) to avoid using the CFD model for parameter estimation. With the tuned lumped kinetic model, CFD predictions agree reasonably with experimental data for $X_{\text{C}_2\text{H}_6}$ (Figure 4.4c), $S_{\text{C}_2\text{H}_4}$ (Figure 4.4d), and product yields (Figure 4.4e), with a mean absolute error (MAE) of 8.2% for $X_{\text{C}_2\text{H}_6}$, 2.8% for $S_{\text{C}_2\text{H}_4}$, and 8.5% for $Y_{\text{C}_2\text{H}_4}$. Deviations at higher operating temperatures are likely due to increased coke formation. Indeed, experiments and simulations under dilute conditions ($< 5 \text{ mol}\%$

C₂H₆ in He), where coke formation is minimal, show very good agreement even at high X_{C₂H₆} (green triangles in Figure 4.4c-e). Overall, the results suggest that the model is adequate but also highlight a future need to incorporate coke formation to improve accuracy.

The mass fraction of C₂H₆ and C₂H₄ near the CFP (Figure 4.4f) shows an almost pure C₂H₆ composition upstream of the CFP, with steep mass fraction gradients near the CFP surface. Kinetic-transport analysis and radial profiles (Figure C.6 and Figure C.7) reveal external mass transfer gradients that increase with increasing temperature, as expected. C₂H₄ forms within 1 mm around the CFP surface and is transferred to the bulk via diffusion and convection. Considering the timescale of ethylene formation is comparable to its consumption in secondary reactions, the system is prone to unwanted secondary reactions at high temperatures. Overall, these results and the above PFR analysis suggest that the CFP reactor is capable of rapid heating but falls short of being an ideal PFR that enhances ethylene yield, and should therefore be expected to be a suboptimal configuration. At the same time, its rapid quenching downstream of the heating tape shortens the reaction zone and is desirable. These features (non-isothermal and rapid quenching) demarcate the tradeoffs of this experimental reactor. We assess these findings via further CFD simulations and experimental work. We assessed performance experimentally for various flow rates, CFP lengths, and temperatures. Due to using He rather than steam and potentially longer residence times than optimal, substantial coking occurred at >1000 °C. At 1000 °C, CFD predicted an optimal Y_{C₂H₄} ~61% with a CFP length of 55 mm and a flow rate of 50 sccm; the experimental Y_{C₂H₄} measured was ~56%. The CFD prediction and experimental result are within the calculated error.

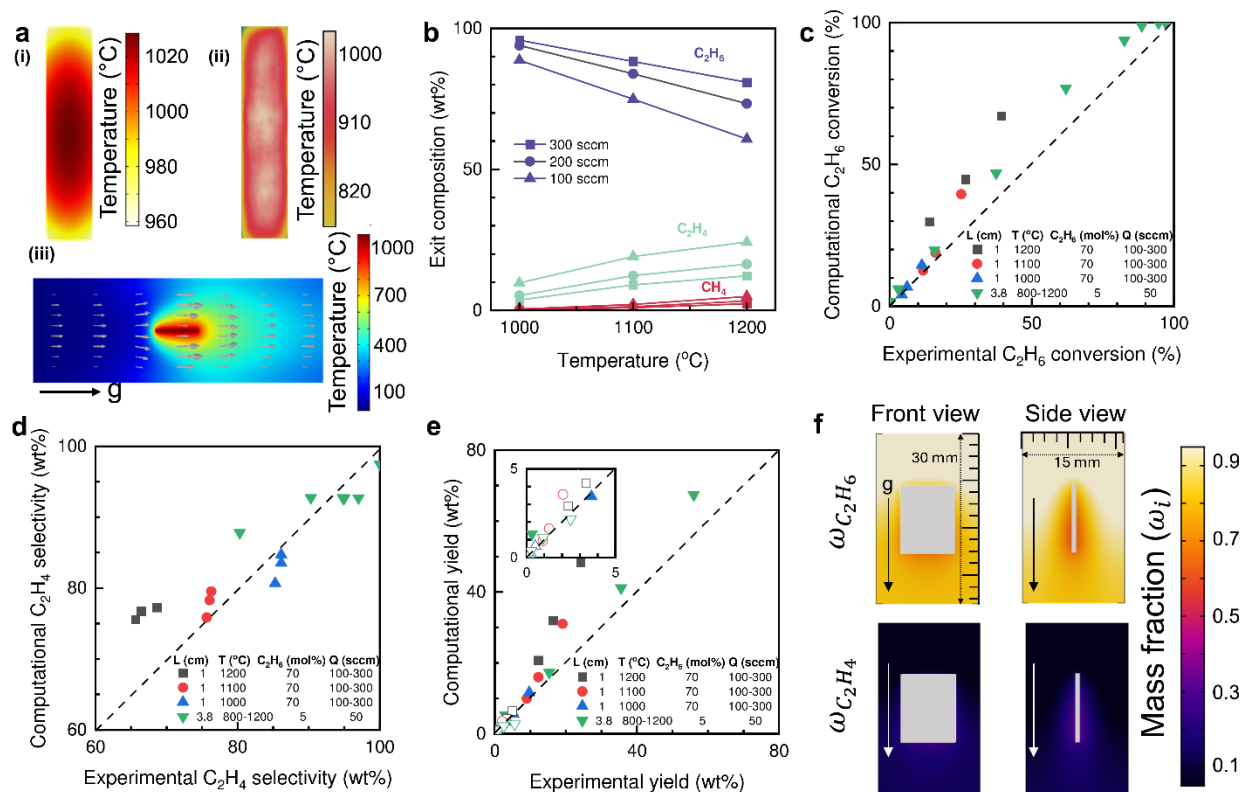


Figure 4.4: Experimental C_2H_6 thermal cracking in the CFP Joule-heated reactor and CFD predictions using the tuned lumped kinetic model. (a) Thermal profile of the heating CFP (wide side view) obtained from (i) CFD and (ii) experimental IR imaging at ~ 18 V, and temperature distribution near the CFP superimposed by velocity streamlines (grey arrows) of CFD simulations (iii) (rotated, narrow side view). (b) Experimental exit composition vs. temperature, for three flow rates and 70 mol% C_2H_6 feed (balance He). Parity plots of CFD-predicted (tuned lumped kinetic model) vs. experimental data for (c) $X_{C_2H_6}$, (d) $S_{C_2H_4}$, and (e) product yield. The inset in panel e shows a zoomed-in view (root mean square error, $RMSE(X_{C_2H_6}) = 0.03$, solid symbols: C_2H_4 ; hollow: CH_4). Further experimental results are in Figure C.4 (CFP temperatures of 1000-1200 $^{\circ}C$ and L of 1 cm), Figure 4.6 (CFP temperatures of 1000-1200 $^{\circ}C$ and L of 3.8 cm), and Figure C.5 (CFP temperature of 800-1200 $^{\circ}C$, L of 3.8 cm, 5 mol% C_2H_6 feed (balance He)). (f) Front and side view of C_2H_6 and C_2H_4 mass fractions in the Joule-heated CFP reactor (excluding He) on a plane cutting the CFP in the middle, at 1100 $^{\circ}C$ with L=1 cm and a total flow rate of 300 sccm. Arrows depict the flow direction. Quantitative radial data are shown in Figure C.7. All data are reported on a dry basis.

Data from our experiments, MKM and CFD predictions at comparable $X_{C_2H_6}$, and incumbent technologies are contrasted in Figure 4.5. $Y_{C_2H_4}$ reached 66% (MKM), 56% (experiment), and 61% (CFD), with a corresponding $S_{C_2H_4}$ of 82%, 71%, and 74% (Figure 4.5a). Industrial steam cracking achieves $Y_{C_2H_4} \sim 53\%$ and $S_{C_2H_4} \sim 79\%$ at 750–900 °C whereas catalytic oxidative dehydrogenation over a Pt foam achieves $\sim 57\%$ yield with 70% selectivity (Figure 4.5b). The Joule-heated reactor with normally diluted feed matches or exceeds these yields without catalysts or oxidants. Dilute experiments in the Joule-heated reactor achieve a higher yield of $Y_{C_2H_4} \sim 63\%$ (Figure C.5). The deviation between CFD and MKM results highlights limitations of the kinetic models (especially omission of direct dehydrogenation of ethylene to acetylene, discussed in Section 4.4.2) and temperature gradients in the Joule-heated CFP reactor compared to a PFR. The deviation between experiments and CFD arises primarily from coke formation at low dilutions. Coke reacts with olefins, especially ethylene, to produce additional coke and methane ($C + C_2H_4 \rightarrow 2C + CH_4$), which explains the higher methane content observed in the experimental product stream. Our findings are consistent with those of Van Goethem et al., [164, 165] who computed a maximum of $Y_{C_2H_4}$ of 67%. Furthermore, their study shows that the highest $Y_{C_2H_4}$ is achieved with a linear concave axial temperature profile, [144] which is indeed characteristic of our CFP-based Joule-heated reactor. [117]

The small mass of the reactor enables rapid heating and gas quenching with a hot heating zone and cold gas, an ideal situation for studying catalytic reactions while quenching gas reactions. Yet, non-isothermal operation is suboptimal for C_2H_6 cracking. We attempted to improve performance by reducing radial gradients through a structured Joule heating element (a monolith). A monolith not only mitigates radial

gradients but also provides an effective pathway for scale-up—especially when combined with scale-out to achieve the required production flow rate. Future studies should leverage advanced data-driven techniques to design the Joule-heating element. CFD simulations for the structured reactor indicate reduced radial temperature gradients as hypothesized (Figure C.8). Immediately downstream of the structured heating element, $Y_{C_2H_4}$ was ~64 wt% compared to 61 wt% for the CFP reactor, due to improved temperature uniformity at 1200 °C and a residence time of ~24 ms. However, the longer downstream cooling of ~1.5 cm than CFP promotes side reactions and reduces $Y_{C_2H_4}$ to 59 wt% (Figure C.8). We suggest that enhanced downstream cooling, e.g., using a transfer line exchanger or other advanced design, can improve the yield.[166] We acknowledge the need to investigate coke formation in these high-temperature, internally-heated crackers, as it directly impacts the heating element's longevity, operational runtime, and potential pressure drop.[167] Currently, the reactor operates in the laminar regime ($Re \sim 10$), with minimal pressure drop. However, future scale-up or changes in element geometry may necessitate a dedicated study on cooling and pressure drop.

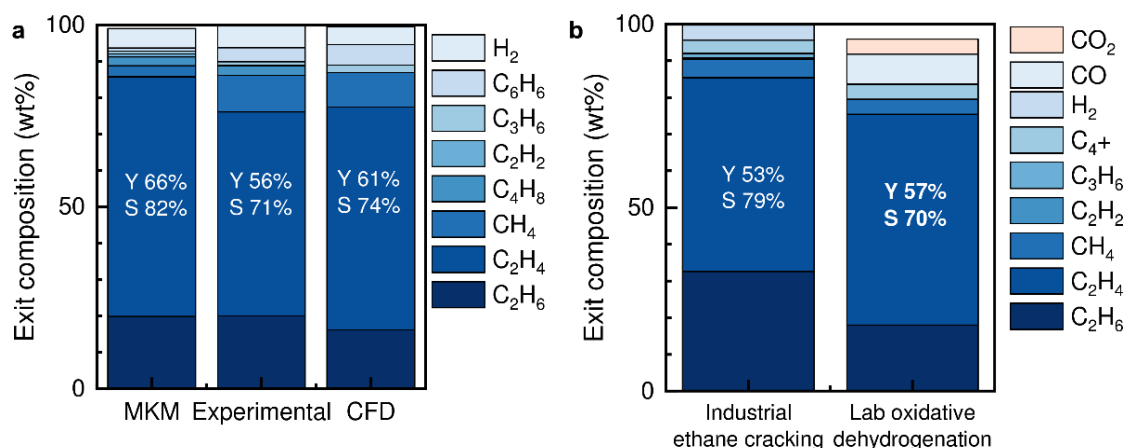


Figure 4.5: Ethylene yield ($Y_{C_2H_4}$) and selectivity ($S_{C_2H_4}$) of this work and existing practices. (a) Predicted and measured data (this work) at high temperatures and short residence times (CFP with $T = 1000\text{ }^{\circ}\text{C}$, $\tau = 10\text{ ms}$, $Q = 50\text{ sccm}$, $L = 55\text{ mm}$, $60\text{ mol\% } C_2H_6$, and $40\text{ mol\% He}$). (b) Literature data for industrial steam cracking ($750\text{-}900\text{ }^{\circ}\text{C}$) and oxidative dehydrogenation over a $2.3\text{ wt\% Pt}$ foam monolith ($C_2H_6/O_2 = 1.7$, $20\text{ vol\% } N_2$, 1.4 atm , $900\text{ }^{\circ}\text{C}$). All data are reported on a dry basis.

4.4.4 Effects of Heating Mode and Operating Parameters on Thermal Cracking

Beyond the steady-state performance of continuous heating, we also investigated the effects of dynamic operation by comparing it with a pulsed heating mode to explore alternative process intensification strategies. Rapid pulse heating (RPH) of temperature, where heating occurs in short bursts when power is switched on, followed by cooling when power turns off, has recently been shown to increase reaction rates, decrease power requirements, and alter selectivity compared to continuous Joule heating (CJH).^[28, 40, 41, 75, 76, 168] Here, we compare these two heating modes for C_2H_6 cracking experimentally under dilute conditions ($5\text{ mol\%}$ of C_2H_6) to minimize the confounding effect of coke formation. CFD simulations for RPH were not performed due to their high computational cost, as experimental data was not encouraging (see below).

As shown in Figure 4.6a, RPH achieves higher $X_{C_2H_6}$ at substantially lower average temperatures than CJH. While CJH requires temperatures approaching 1200 °C for significant conversion for a CFP length of 3.8 cm and 50 sccm, RPH demonstrates comparable performance at average temperatures of 800 °C. This efficiency advantage is also reflected in the power requirements (Figure 4.6b); RPH reaches equivalent conversion with half the input power of CJH. The product selectivity differs (Figure 4.6c). Moderate conversions favor C_2H_4 production for both methods. At high conversions, CJH maintains high C_2H_4 selectivity (>80%), while RPH promotes C_2H_2 and byproducts. The $Y_{C_2H_4}$ for RPH peaks at moderate power inputs (~70 W) before declining at higher powers due to secondary reactions (Figure 4.6d).

Kinetic analysis by fitting a power law rate expression, $r=a \times P^n$, using partial pressure experiments reveals that CJH has higher ethylene formation rate ($a = 0.58$ vs. $0.28 \text{ mmol kPa}^{-n} \text{ h}^{-1}$), whereas RPH significantly promotes byproducts with a rate constant which is higher than CJH for methane, acetylene, and aromatics by 5×, 19×, and 35×, respectively. The observed reaction orders ($n \approx 1$ for ethylene, $n \approx 0.82$ -0.84 for acetylene, and $n \approx 1.22$ -1.26 for methane) indicate that tuning the ethane partial pressure could enhance selectivity (Figure C.10). Steam dilution appears to have a slight effect on conversion and selectivity with small CO formation (Figure C.11).

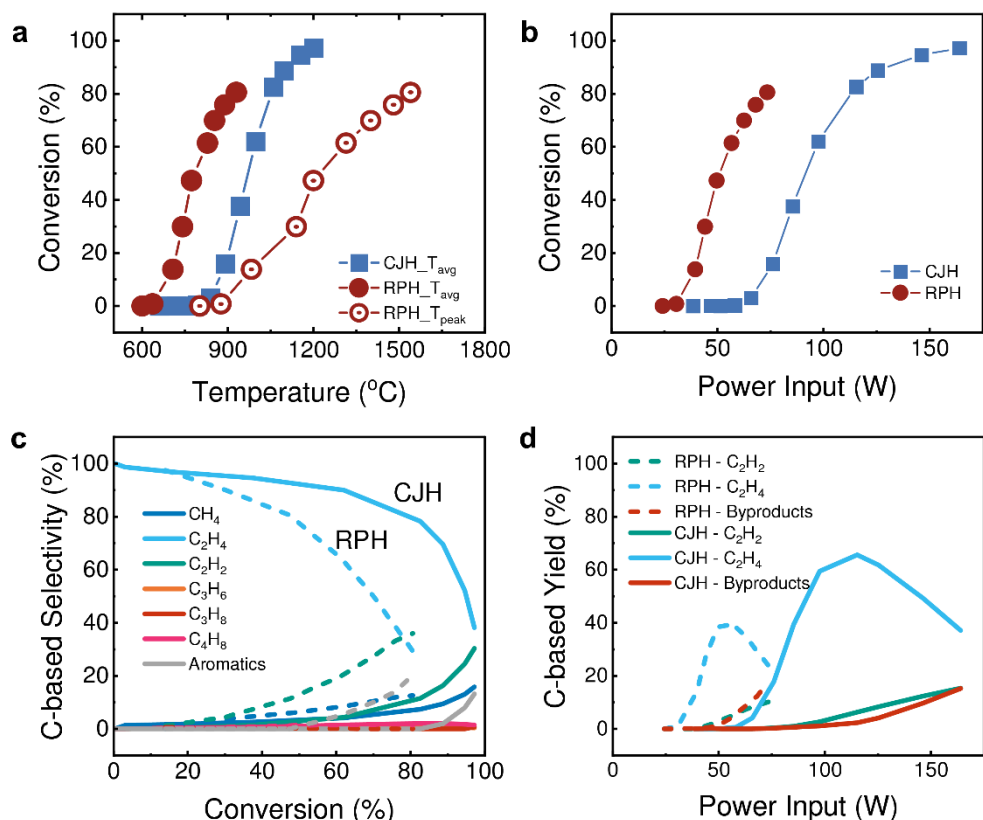


Figure 4.6: Heating mode performance comparison of experimental CFP reactor. (a) $X_{C_2H_6}$ vs. temperature, (b) $X_{C_2H_6}$ vs. power input for RPH and CJH over a CFP of length 3.8 cm, 5 mol% C_2H_6 in He, and total flow rate of 50 sccm. (c) $S_{C_xH_y}$ vs. $X_{C_2H_6}$ and (d) $Y_{C_xH_y}$ vs. power input for RPH (dashed lines) and CJH (continuous lines). Byproducts include CH_4 , C_3H_6 , C_4H_8 , and C_6H_6 . All data are reported on a dry basis.

4.4.5 Technoeconomic Analysis (TEA) and Life-cycle Assessment (LCA)

With a comprehensive understanding of the reactor's technical performance, we proceeded with a techno-economic analysis (TEA) and life-cycle assessment (LCA) to evaluate its commercial viability and environmental impact against the industry benchmark. We conducted TEA using Aspen (Figure C.12) for Joule heating at 1000 °C for a product stream corresponding to different scenarios: a selectivity of 80% (MKM- Sc_2H_4), a conversion of ~65% (MKM- $X_{C_2H_6}$), or the optimal experimental

exit composition (Exp-Opt), using electricity derived from natural gas and compared to conventional processing (Figure 4.7). The associated yield of ethylene is ~53% (conventional steam cracking), ~66% (MKM- $\text{S}_{\text{C}_2\text{H}_4}$), 56% (MKM- $\text{X}_{\text{C}_2\text{H}_6}$), and 56% (Exp-Opt achievement). For industrial-grade C_2H_4 purity (99.9%), processes operate at 30 wt% steam; MKM- $\text{S}_{\text{C}_2\text{H}_4}$ operates with 40 wt% steam to reduce acetylene and achieve the desired purity.

The Total Capital Investment (TCI) of Joule heated systems with MKM- $\text{S}_{\text{C}_2\text{H}_4}$ and MKM- $\text{X}_{\text{C}_2\text{H}_6}$ compositions is lower by ~23% (\$242–254 M from \$317 M) due to eliminating the furnace whereas Exp-Opt is comparable to industry due to long distillation columns (Figure 4.7a). The Total Cost of Manufacturing (TCM) increases (\$504–586 M/y from \$404 M/y) due to the elevated electricity cost (\$145–154 M/y compared to \$37.6 M/y), driving up the Minimum Selling Price (MSP) to \$815–960/t from \$680/t (Figure 4.7a-b). MKM- $\text{S}_{\text{C}_2\text{H}_4}$ shows the highest TCM due to increased steam dilution, requiring larger water separation units and more water removal utilities (Figure 4.7b). Despite a lower total energy duty (Figure 4.7c), the electricity-driven systems give higher TCM due to electricity cost. The net specific energy is reduced from 14.7 to 7.4–7.5 GJ/t, i.e., by ~50%, for the MKM cases and from 14.7 to 9.7 GJ/t, i.e., by ~30%, for Exp-Opt due to higher intrinsic heating efficiency (85-95% vs. 60%[20]) (Figure 4.7d). CH_4 separation from the C_2H_4 -rich reactor exit stream incurs the highest utility cost due to operating below -100 °C. While MKMs lower CH_4 formation, the experimental composition contains significant CH_4 due to lack of reactor optimization, leading to elevated separation costs. Because this work evaluates a low-Technology Readiness Level, internally Joule-heated reactor design, the TEA results carry inherent uncertainty related to capital costs, operational stability, material

lifetime, and scalability. Our analysis shows that the industrial electricity price and the operational lifetime/replacement cost of the CFP heating element are the dominant factors determining the MSP and the key levers constraining the viability of internal Joule-heated crackers. A systematic sensitivity analysis of these parameters, along with other capital and operating assumptions, would be valuable in future studies to better define the economic outlook.

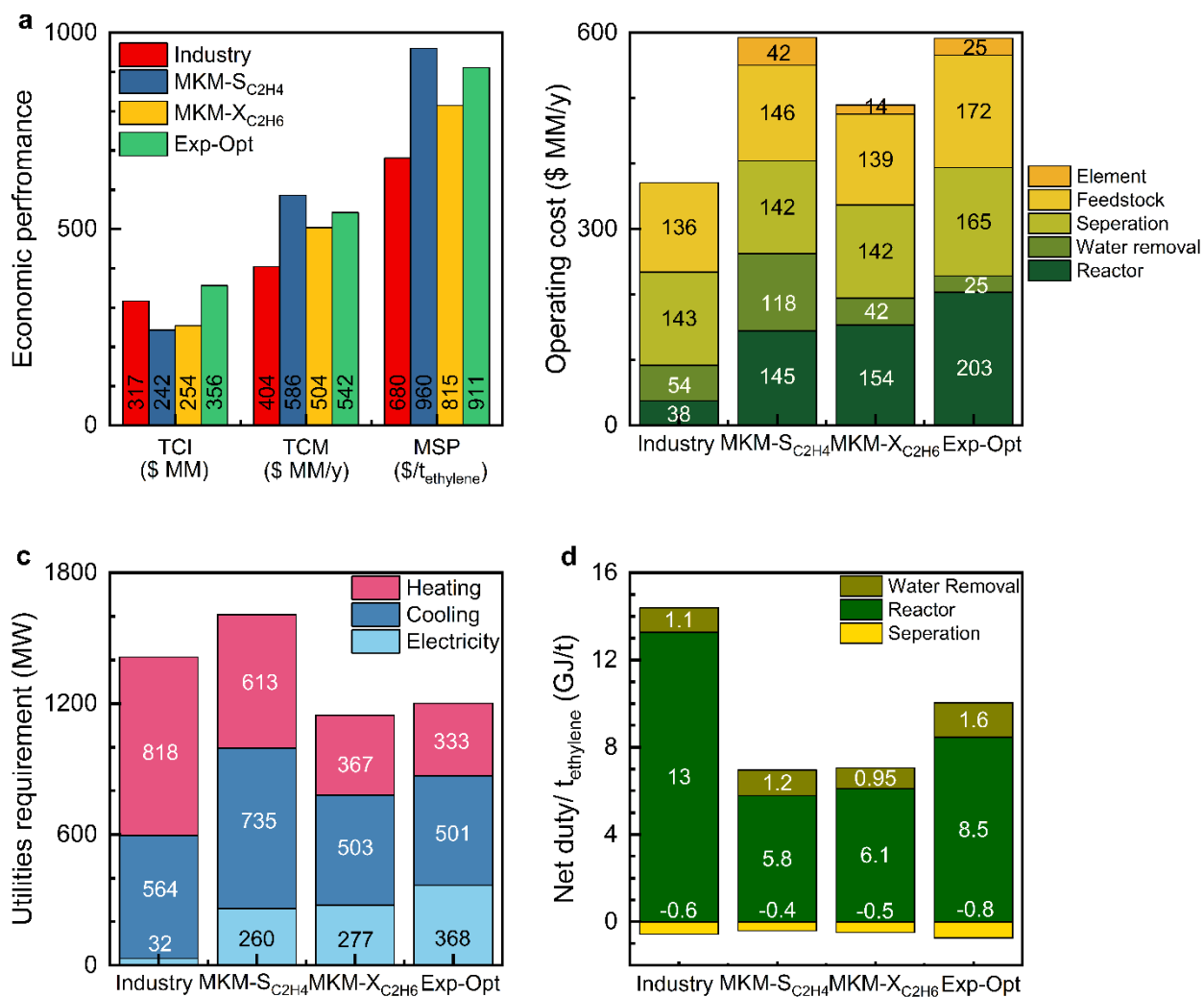


Figure 4.7: TEA of industrial benchmark, MKM-predicted product yields in an ideal PFR, and experimentally attained product yield. (a) Total capital investment (TCI), total cost of manufacturing (TCM), and minimum selling price (MSP). (b) Operating costs. (c) Breakdown of utilities. (d) Net energy duty. Positive (negative) numbers represent net heating (cooling).

LCA quantified the Global Warming Potential (GWP); Joule-heated thermal cracking using natural gas-derived electricity leads to comparable emissions (3.97 vs.

the benchmark of 4.12 kg CO₂-eq/kg C₂H₄) (Figure 4.8a) for MKM-XC₂H₆. Comparable emissions result from improved energy efficient Joule-heated reactors. Current experimental data leads to 25% higher emissions. GWP values would decrease further with flowsheet optimization and steam production credits.[3] *Chen et al.[16]* reports ~0.6-0.8 kgCO₂-eq/kgC₂H₄ credits from high-pressure steam generation, potentially lowering GWP to ~3.3, 4.1, 3.2, 4.4 kgCO₂-eq/kgC₂H₄ for industry, MKM-SC₂H₄, MKM-XC₂H₆, and Exp-Opt respectively. Therefore, our GWP values should be viewed as high.

The electricity source strongly influences the GWP and MSP (Figure 4.8b-c). Coal-derived electricity increases the GWP to 5 kg CO₂-eq/kg C₂H₄ and the MSP to \$1049/t for MKM-XC₂H₆. Onshore wind reduces GWP to 2.4 kg CO₂-eq/kg C₂H₄ and achieves near-parity MSP (\$694/t vs. \$680/t). Offshore wind, solar, and hydropower yield ~2.4 kg CO₂-eq/kg C₂H₄ with moderate MSP increases (\$710–835/t). These results highlight that renewable electricity not only reduces emissions but can also improve economic feasibility. MKM-XC₂H₆ powered by wind or hydropower reduces emissions by 40%. These findings align with *Gu et al.,[18]* who reported that electrified steam cracking (E-SC) can reduce CO₂ emissions by ~ 10% compared to conventional steam cracking. *Shin et al.[46]* further demonstrated the potential for achieving negative emissions by implementing electrified crackers. TEA and LCA of other electrified olefin production strategies have also shown promising outcomes.[169-171]

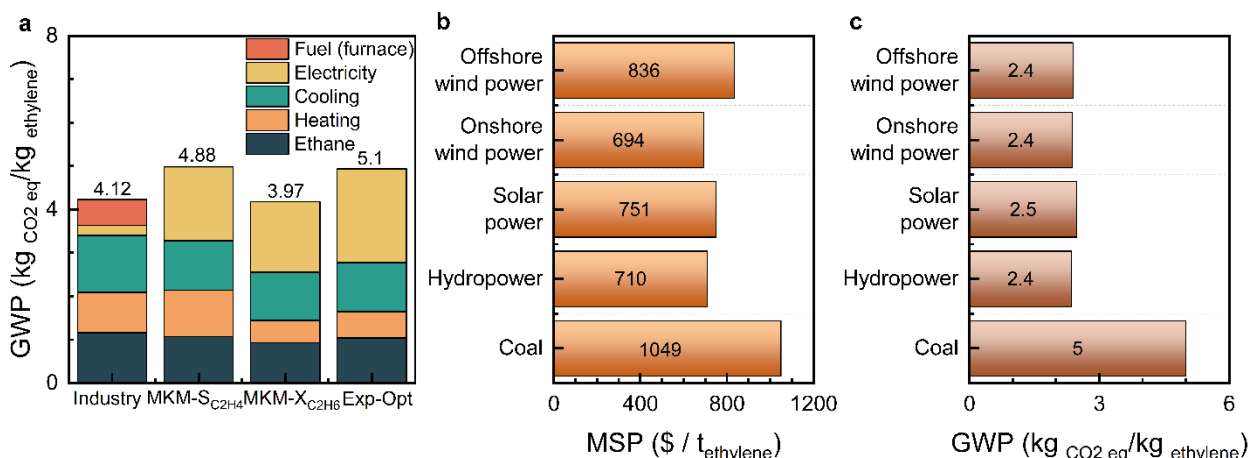


Figure 4.8: LCA of the industrial benchmark and Joule-heated reactors. (a) GWP breakdown. Numbers indicate the total GWP. (b) MSP for MKM-X_{C₂H₆} using different sources of electricity. Numbers indicate the MSP. (c) GWP for MKM-X_{C₂H₆} using different sources of electricity. Numbers indicate the GWP.

4.5 Conclusion

C₂H₄ is one of the most important building blocks of the petrochemical industry. Current C₂H₆ steam cracking is energy-intensive and is powered by indirect heating, which limits the choice of wall materials to withstand high temperatures. Efforts are underway to electrify steam crackers. This work explored the potential of direct, internal Joule heating to provide precise thermal control and explore inaccessibly high temperatures imposed by wall limitations of externally heated reactors.

We employed a lumped and a microkinetic model to identify optimal operating conditions and compared CFD simulations and experimental data in a carbon fiber paper (CFP) reactor using the original and a tuned lumped kinetic model more suitable for higher temperatures and lower residence times. Even though kinetic models exhibited quantitative differences in optimal ethylene yield, they revealed higher

ethylene yields than the incumbent technology through higher temperatures and shorter residence times than industrial conditions. The difference between the lumped kinetic model and the microkinetic model results was primarily due to the omission of direct dehydrogenation of C_2H_4 in the former and potential uncertainty in model parameters. The discrepancies between CFD and the microkinetic model results mainly stem from the non-isothermal nature of our reactor and potential errors in the kinetics under these conditions, e.g., the onset of coke precursors. Isothermal operation maximizes ethylene yield. Hot gases react downstream of the hot zone in colder regions (a longer residence time), deteriorating selectivity. Microkinetic analysis reveals ultra-short residence times quench radical chain propagation, suppressing byproduct formation, especially methane, acetylene, and aromatics. It is thus important to quench the chemistry downstream of the hot zone as fast as possible. The CFP reactor is not isothermal but achieves fast (~ 1 mm) quenching, striking a balance in performance. CFD simulations in a Joule-heated monolith showed reduced radial temperature gradients, higher ethylene yield than the CFP reactor, and a clear need for downstream quenching.

We identified an optimal operational window (1000–1150 °C, <10 ms). Microkinetic modeling in an isothermal PFR predicts an optimal ethylene yield of 66%. For small scale non-isothermal reactors, we predicted a maximum ethylene yield up to 64% in a monolith and 61% in the CFP. We measured a yield of 56% in CFP experiments, surpassing the industrial benchmark of 53%. Experiments revealed that the C_2H_4 selectivity and yield of continuous Joule heating outperform those of pulsed heating, because short exposures to high temperatures promote acetylene, aromatics, coking, and methane despite the higher overall rate of ethane conversion and lower

power of pulsing. Future work should address long-term operational challenges, including coke formation and its impact on sustained reactor performance. In a forthcoming manuscript, we also examine the stability of the heating element under exposure to mild oxidants (such as steam and CO_2) at very high temperatures. Economic and environmental evaluations indicated a substantial reduction in capital expenditure and energy use; however, operational costs are high when using electricity generated from natural gas. Joule-heated C_2H_6 crackers powered by renewable energy or nuclear energy can be economically competitive, enabling advanced manufacturing for the petrochemical industry. Still, cheap electricity in large amounts, beyond what is currently available, would be a prerequisite. The comprehensive findings of this work—spanning from fundamental kinetics to economic feasibility—holistically establish internal Joule heating as a powerful, viable pathway toward decarbonized and intensified olefin production.

Chapter 5

INSIGHTS INTO MIXING OF ON-ISOTHERMAL MELTI-POLYMER MELTS

5.1 Contribution

The validation experiments in this chapter are performed by Christine Oberhausen. Rheology measurements were done by Alex H. Balzer. The Carreau-Arrhenius model fitting is done by Devin Dabagian and Maxwell Bobbin. All other work is done by this thesis' author. This chapter is based on under review work in Chemical Engineering Journal.

5.2 Introduction

Catalytic chemical recycling offers a promising pathway to address the growing challenge of plastic waste.[50, 172, 173] Polyolefins, such as polyethylene (PE) and polypropylene (PP), account for more than half of global plastic production, yet they remain largely unrecycled due to their chemical inertness and the complexity of post-consumer waste streams.[47] A major challenge arises from the widespread use of mixed plastics and multilayer films (MLFs), which combine polymers with different chemical compositions and physical properties. These heterogeneous materials complicate catalyst design and severely limit heat and mass transfer within a reactor medium.[50, 174] In addition, physical separation of multilayer and mixed plastics is technically difficult and economically prohibitive, motivating the development of reactors capable of processing such materials in a single step.[47, 175]

Although substantial progress has been made in catalyst development for plastic recycling, comparatively little attention has been paid to the reaction-engineering challenges associated with processing highly viscous polymer melts.[53] Polyolefin melts exhibit strong temperature-dependent, non-Newtonian behavior, leading to complex flow fields, poor heat transfer, and the formation of stagnant regions in stirred tank reactors.[26, 55, 56, 58, 59, 176-179] In industrial polymer processing, twin-screw extruders are widely used because they can provide strong shear and efficient mixing over a broad range of operating conditions. However, their complexity and continuous-processing design can make them less convenient for mechanistic studies and small-scale catalytic screening, motivating the use of impellers.[178, 180, 181] Consequently, stirred tank reactors remain an attractive alternative, provided that their hydrodynamic limitations can be addressed.

Recent studies have highlighted the critical role of mixing in achieving desired selectivity and catalyst utilization. *Jaydev et al.* demonstrated its importance in high-density polyethylene (HDPE) hydrogenolysis, but these investigations have largely been confined to small-scale, single-polymer systems.[53] Such conditions do not directly relate to multipolymer feeds and non-isothermal operation in close-clearance impellers that are commonly employed for highly viscous non-Newtonian melts.[174] Moreover, prior work has emphasized the importance of accurate viscosity modeling, which is required for systematically comparing impeller designs and developing reactor-level understanding of polymer-melt mass and heat transport behavior.[57, 182-187] In addition to shear-thinning at high shear rates, polymer melts also exhibit viscoelasticity, which introduces elastic stresses that can alter flow patterns and affect power consumption.[55] Therefore, identifying operating conditions where

viscoelastic effects become sufficiently weak is important, as it enables the use of generalized Newtonian models for reactor-scale analysis and the development of preliminary design guidelines.[188]

In this work, we integrate rheological measurements, modeling, CFD, and experiments to develop a reactor-scale framework that can be utilized to gain insights into multi-polymer melt processing. Temperature- and shear rate-dependent viscosities of representative polymers are measured, and two surrogate polymers (P_{LD} and P_{HD}) are assumed by fitting the viscosity data using the Carreau-Arrhenius model to capture non-isothermal, generalized Newtonian, shear-thinning behavior. CFD simulations on a two-dimensional (2D) system are first used to gain preliminary insights into the impact of viscoelasticity using P_{LD} and P_{HD} as captured by the Phan-Thien and Tanner (PTT) model on flow dynamics and identify approximate operating conditions that suppress elastic instabilities for weakly viscoelastic, minimally entangled polymer melts. Within these regimes, where elastic contributions are assumed to be sufficiently weak, a generalized Newtonian approximation is adopted as a tractable first step toward understanding polymer-melt mixing and informing the development of more comprehensive viscoelastic reactor models. Three-dimensional (3D) CFD simulations employing the Carreau-Arrhenius model are then used to evaluate key impeller performance metrics, including mixing time, cavern volume, power utilization, circulation velocity, and polymer-polymer interfacial area across various close-clearance, multi-impeller configurations. Experimental measurements validate model and parametric studies map design space and establish operational guidelines for chemical recycling of highly viscous, shear-thinning polymers in stirred-tank reactors.

5.3 System description, methods, and material properties

5.3.1 System description

Figure 5.1 illustrates the mesh, mixing vessel geometry, and impeller geometries evaluated in this study. The vessel height was designed to accommodate 2 g of molten polymer, either low-density polyethylene (LDPE) or HDPE. This mass was selected to maintain consistency with commonly used conditions reported in prior experimental studies.[49, 50] To investigate the influence of impeller design on the mixing of highly viscous polymer melts, several impeller configurations were modeled and compared, including a magnetic stir bar, a two-blade anchor impeller, an anchor impeller combined with a coaxial flat-blade turbine (FBT), and an anchor impeller combined with a coaxial pitched-blade turbine (PBT). We also analyzed a four-blade anchor impeller with dimensions identical to the two-blade configuration, augmented by an additional arm oriented perpendicular to the original.

3D geometries were used to analyze generalizable Newtonian inelastic shear-thinning polymer behavior and capture detailed flow features in surrogate polymers associated with impeller motion. 3D simulations are important to capture asymmetric impellers and mixing.

To reduce computational cost for simulations involving non-Newtonian viscoelastic polymers, 2D simplified geometries were also employed.[189] A coaxial cylindrical representation was used for single-phase mixing simulations, whereas an axisymmetric 2D geometry was adopted for immiscible polymer-polymer mixing. The axisymmetric approximation captures the dominant shear and normal stress gradients while significantly reducing computational cost.

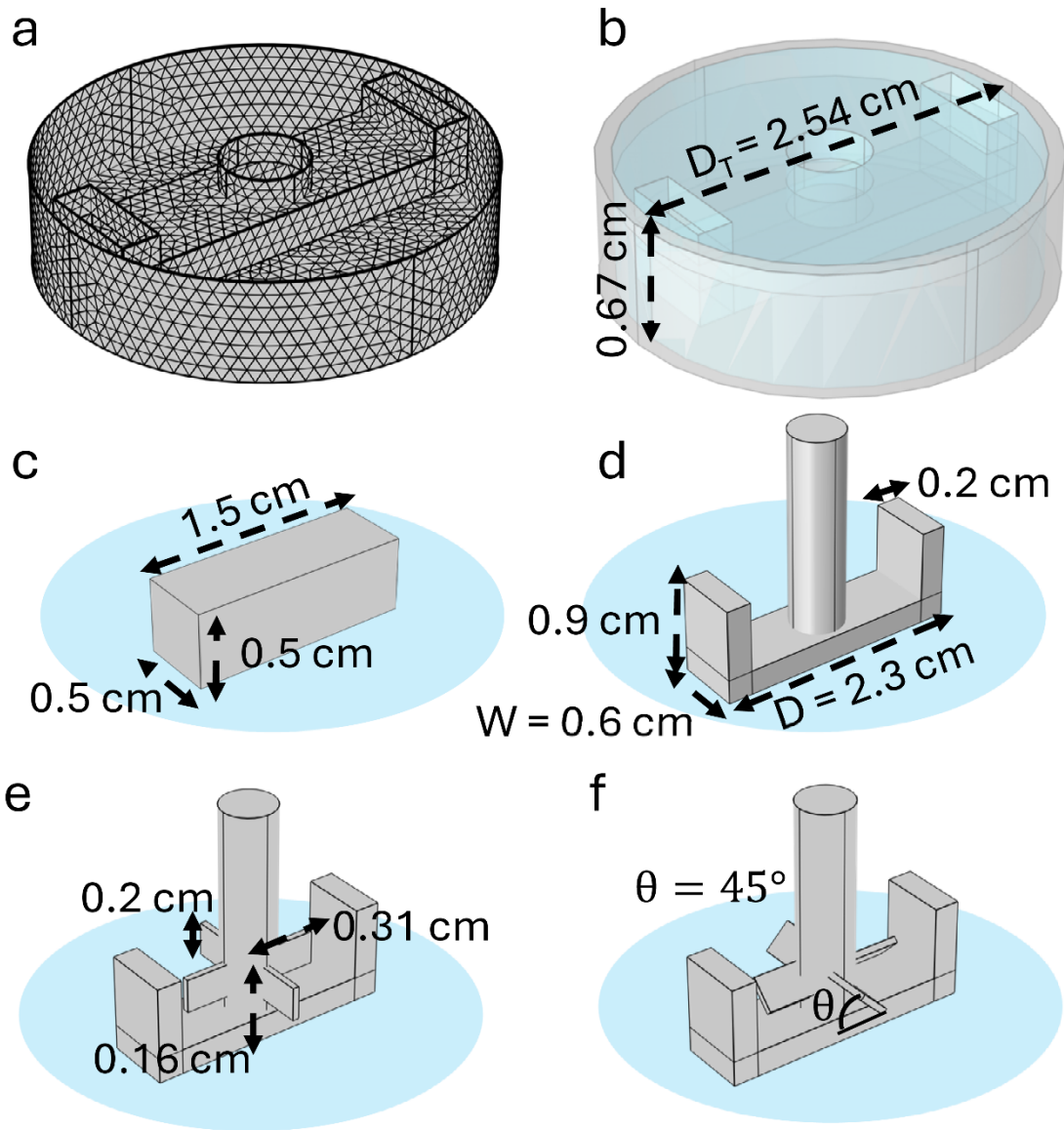


Figure 5.1: Schematic of the mesh discretization and impellers and mixing vessel. (a) Mesh discretization with a two-blade anchor impeller. (b) Mixing vessel geometry. (c) Magnetic stirrer. (d) Two-blade anchor impeller. (e) Anchor + flat blade turbine (FBT). (f) Anchor + pitch blade turbine (PBT).

5.3.2 Rheological experiments and materials

Viscosity measurements were collected for representative polymer samples of LDPE (weight-average molar mass (M_w) ~ 71 kg/mol, number-average molar mass (M_n) = 10 kg/mol, dispersity ($\mathcal{D}$) = 7.1, Sigma Aldrich) and HDPE ($M_w \sim 60$ kg/mol, $M_n = 12$ kg/mol, $\mathcal{D} = 5.0$, Sigma Aldrich). The rheological behavior of these polymers was investigated using a TA Instruments strain-controlled, ARES G2 rheometer. Samples were loaded into pre-heated (200 °C) test geometry (25-mm-diameter parallel plates) and then pressed and trimmed to a thickness of 1 mm. A 60 s, 1 s^{-1} pre-shear step was performed prior to testing to remove any stresses induced during loading. Oscillatory frequency sweeps were conducted from 0.1 to 500 rad s^{-1} at strains within the linear viscoelastic regime (as determined by amplitude sweeps) at temperatures ranging from 200 °C to 300 °C (LDPE) or 150 °C to 300 °C (HDPE). All experiments were conducted in a nitrogen atmosphere. The complex viscosity from oscillatory frequency sweep data was transformed into shear viscosity using the Cox-Merz rule.

5.3.3 Steady-shear viscosity model

The dynamics of the entanglement network govern the flow behavior of polymer melts. At equilibrium, polymer chains remain as randomly entangled coils, generating a high zero-shear viscosity (η_0), which remains constant at low shear rates ($\dot{\gamma}$). [55, 190] At higher shear rates, chain alignment, sliding and/or partial disentanglement dominate, resulting, among other effects (such as memory and elasticity), in a decrease in viscosity (i.e., shear thinning). [191] The $\dot{\gamma}$ at which the polymer shows shear thinning behavior is the inverse of the characteristic Carreau timescale (λ_c). [190, 192, 193]

For a given temperature, we modeled the shear rate-dependent viscosity, also known as apparent viscosity ($\eta(\dot{\gamma})$), using the simplified Carreau model (eq. 5.1) to capture the generalizable Newtonian shear thinning flow behavior:

$$\eta(\dot{\gamma}) = \eta_0 \times (1 + (\lambda_c \dot{\gamma})^2)^{\frac{n-1}{2}} \quad (5.1)$$

wherein n is the power-law index that describes the degree of shear thinning. We assumed n , which characterizes the degree of shear-thinning behavior, to be temperature independent, which is consistent with time-temperature superposition principles. Furthermore, we incorporated the temperature dependence of η_0 and λ_c via Arrhenius-type relationships.

$$\ln(\eta_0) = \ln(A_{\eta_0}) + \frac{E_{\eta_0}}{T} \quad (5.2)$$

$$\ln(\lambda_c) = \ln(A_\lambda) + \frac{E_\lambda}{T} \quad (5.3)$$

Here, E_{η_0} and E_λ represent the fluid activation energies associated with viscous flow and Carreau relaxation time, respectively, reflecting the sensitivity of these properties to temperature. A_{η_0} and A_λ are pre-exponential fitted parameters that represent the corresponding values at extremely high temperatures or the minimum value attainable.

In this study, two surrogate polymer models, P_{LD} and P_{HD} , are introduced to minimize computational time and represent LDPE and HDPE, respectively, based on their measured viscosity behavior. Both surrogates are assumed to exhibit negligible elastic and memory effects, and are therefore modeled using a single relaxation mode. Hence, these surrogate polymer models are similar to those of highly viscous shear-thinning liquids. A global fit was performed on the temperature-dependent viscosity data of LDPE and HDPE to determine the five model parameters (A_{η_0} , A_λ , E_{η_0} , E_λ , n)

for P_{LD} and P_{HD} . We carried out the optimization using the trust region reflective (TRF) algorithm via the SciPy library in Python. [194]

To ensure a robust fit and avoid local minima, we adopted a staged initialization method. First, we fit individual Carreau models at each temperature to estimate $\ln(\eta_0)$ and $\ln(\lambda_c)$. We then linearly regressed these estimates against inverse temperature ($1/T$) to derive physically meaningful initial guesses for the Arrhenius parameters. Finally, we minimized the sum of squared logarithmic residuals between the model-predicted ($\eta_{pred,i}$) and experimentally ($\eta_{exp,i}$) obtained steady-shear viscosity values to obtain the optimal parameter set.

$$\min_{\theta} \sum_i (\ln(\eta_{pred,i}) - \ln(\eta_{exp,i}))^2 \quad (5.4)$$

We used logarithmic residuals to account for the multi-order variation in viscosity. We enforced non-negative activation energies ($E_{\eta_0} \geq 0$, $E_{\lambda} \geq 0$) and realistic shear-thinning behavior ($0 \leq n \leq 1$) as physical constraints.

5.3.4 Computational fluid dynamics

We conducted computational fluid dynamics (CFD) simulations using COMSOL Multiphysics 6.2.[115] For the 2D viscoelastic flow analysis, the laminar flow module was used because of high viscosity of the polymer melt.[56] The laminar flow model was used to compute the velocity and pressure fields by solving the modified Navier-Stokes equation (eq. 5.5) and the continuity equation for incompressible fluids (eq. 5.6), with viscoelastic effects incorporated using the linear Phan-Thien-Tanner (PTT) model (eq. 5.8).[105, 117, 190, 195]

$$\frac{d\rho u}{dt} + \nabla \cdot (\rho u \times u) = \nabla \cdot [\mathbf{K} + \mathbf{T}_e] - \nabla p + \rho g + F \quad (5.5)$$

$$\rho \nabla \cdot \mathbf{u} = 0 \quad (5.6)$$

$$\mathbf{K} = \mu_s (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \quad (5.7)$$

$$\lambda \frac{\Delta \mathbf{T}_e}{\Delta t} + \left(1 + \alpha_e \frac{\lambda}{\eta_0} \mathbf{T}_e \right) \mathbf{T}_e = \eta_0 (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \quad (5.8)$$

$$\frac{\Delta \mathbf{T}_e}{\Delta t} = \frac{\partial \mathbf{T}_e}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{T}_e - \nabla \mathbf{u} \cdot \mathbf{T}_e - \mathbf{T}_e \cdot \nabla \mathbf{u}^T \quad (5.9)$$

In eq. 5.5, ρ denotes the density, $\mathbf{u}$ is the velocity, p is the pressure, $\mathbf{g}$ is the gravitational acceleration, $\mathbf{K}$ is the viscous stress tensor, $\mathbf{T}_e$ is the elastic stress tensor, λ is the characteristic relaxation time, and $\mathbf{F}$ is the body force. In eq. 5.7, μ_s is the solvent viscosity, and in eq. 5.8, α_e is the mobility. Despite being a solvent-free system, μ_s is used for better convergence and to capture infinite shear viscosity. α_e was estimated by fitting the polymer viscosity data under the assumption of a single relaxation time, approximated as λ_c . While this single-mode representation is a simplification, because polymer melts typically exhibit a spectrum of relaxation times, it captures one of the viscoelastic responses relevant to the operating conditions considered here. A multi-mode description would improve accuracy, particularly for high-molecular-weight systems but would significantly increase computational cost. Therefore, a single relaxation time framework was adopted to enable tractable simulations while preserving the key trends required for initial reactor-scale analysis. To ensure convergence, the discrete Elastic-Viscous-Split-Stress (DEVSS) method was also employed.[196]

For the 3D inelastic generalizable Newtonian flow analysis, the laminar flow module was again used to compute the velocity and pressure fields by solving the Navier-Stokes and the continuity equations for incompressible flow, with shear-

thinning behavior captured using the Carreau-Yasuda viscosity model (eq. 5.1) instead of the viscoelastic PTT model. The Carreau-Yasuda model works under the assumption that the elastic contributions are negligible ($\lambda \frac{\Delta T_e}{\Delta t} \sim 0$), and under these conditions, the stress divergence term simplifies to $\nabla \cdot [\mathbf{K} + \mathbf{T}_e] = \eta(\dot{\gamma}) \nabla^2 u$. [190] Furthermore, inertial effects are negligible due to the high viscosity of polymer melts, and the flow operates in the creeping-flow regime; accordingly, the convective inertia term ($\nabla \cdot (\rho \mathbf{u} \times \mathbf{u}) = 0$) was neglected. The governing momentum equation (eq. 5.5) is thus reduced to eq. 5.10. [59, 197]

$$\frac{d\rho u}{dt} = \eta(\dot{\gamma}) \nabla^2 u - \nabla p + \rho g + F \quad (5.10)$$

and solved in conjunction with the continuity equation and the Carreau-Yasuda model. To resolve the temperature gradients, we coupled the heat transfer module with the flow solver. Heat generation arises primarily from two sources, namely, dissipation at constant pressure (Q_p) and viscous heat dissipation in the fluid (Q_{vd}), which contribute to the energy balance (eq. 5.11). [183]

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \nabla T = -\nabla(\kappa \nabla T) + Q_p + Q_{vd} \quad (5.11)$$

$$Q_p = -\left(\frac{1}{\rho}\right) \frac{\partial \rho}{\partial T} T \left(\frac{\partial p}{\partial t} + \mathbf{u} \cdot \nabla p\right) \sim 0 \quad (5.12)$$

$$Q_{vd} = [\mathbf{K} + \mathbf{T}_e] : \nabla \mathbf{u} \quad (5.13)$$

In eq. 5.11, C_p is the specific heat, T denotes the temperature, and κ is the thermal conductivity. Q_p was assumed to be negligible because incompressible fluid is assumed throughout this work. The surrogate polymer melt was modeled using a rotating domain with a prescribed rotational speed corresponding to a constant impeller rotation rate (N , rev s⁻¹). The impeller blades and shaft were modeled using a sliding-

wall boundary condition, while the container walls and bottom were modeled as a stationary no-slip boundary condition.[189, 198]

The top surface of the polymer melt was defined as an open boundary with constant normal stress, consistent with experimental conditions in which additional polymer mass (Δm) was used to maintain a stable free surface for a nominal 2 g melt (refer to Section D.1 for more details). To emulate the thermal environment of a Parr reactor, the outer vessel walls were maintained at a constant temperature (T_{wall}). Heat loss from the free surface was modeled using a constant heat flux boundary condition, representing an enclosed reactor with limited heat exchange with the surroundings.

To quantify mixing and concentration uniformity, the transport of diluted species module was incorporated by solving eq. 5.14 to track the evolution of a passive tracer within the melt.[189]

$$\frac{\partial c}{\partial t} - \nabla \cdot (D_0 \nabla c) + u \cdot \nabla c = 0 \quad (5.14)$$

In eq. 5.14, c is the tracer concentration and D_0 is the diffusion coefficient ($10^{-9} \text{ m}^2/\text{s}$).[189] We introduced tracer at the top surface of the polymer melt at $t = 0$. Mixing progress was monitored using four probes located at different positions within the domain. Steady state was considered to be reached when the concentrations measured at all probe locations converged to the same value. Previous work confirmed that the steady-state results are independent of the tracer injection location.[189]

To capture the flow patterns and polymer-polymer interface evolution, a two-phase phase-field model was employed.[105] Phase-field defines the parameters controlling interface thickness and mobility parameters. A contact angle of 90° was specified to represent neutral wetting conditions at the vessel walls and the impeller.

At $t = 0$, the denser surrogate polymer (P_{HD}) was initialized below the lighter surrogate polymer (P_{LD}). Mesh-independence tests were performed to ensure that the simulation results were insensitive to grid resolution and discretization size. The material properties used in the simulations are summarized in Appendix D (Table D.1).[55]

5.3.5 Power validation experiments

Power validation experiments were conducted with a Parr Series 4565 100 mL Mini Reactor, with a 25 mL volume reactor vessel. A custom two-blade anchor impeller was fabricated with dimensions identical to those which were modelled (Figure 5.1d). Temperature and stirring rate were monitored and controlled with a Parr 4848 reactor controller. Percent total motor output at varying stir rates was monitored using SpecView software and converted to power (Watts) using the maximum power rating of the stirrer motor (1/8 hp = 93.2 Watts). No-load power losses were measured with He in the reactor vessel at 300 °C, which were then subtracted from the measured motor outputs required to stir LDPE at 300 °C. Motor outputs were recorded by increasing the stir rate stepwise from 0 to 300 rpm in 20-100 rpm increments and holding after each increment for at least 1 min.

5.3.6 Performance metrics

We calculated the power and torque required for each impeller by computing the inverse torque acting on the impeller surfaces due to the pressure and viscous forces. Inverse torque was calculated using the method reported by *Takahashi et al.*[199, 200] Power is reported using the dimensionless power number (N_p) defined as

$$N_p = \frac{P_{tot}}{\rho N'^3 D^5} \quad (5.15)$$

Here, P_{tot} is the total power required by the impeller, N' is the effective rotational speed, and D is the impeller diameter. For anchor impellers and magnetic stirrers, $N' = N$, wherein N is the rotational speed of the shaft/motor. In contrast, for co-axial impellers such as anchor + PBT and anchor + FBT, $N' = (1 + P_a/P_{tot})N$, wherein P_a is the total power consumed solely by the anchor impeller, and D corresponds to the diameter of the attached turbine (D_c). [201, 202] We also evaluated other key dimensionless numbers, such as the Reynolds (Re), pseudo-Deborah (De^*), pseudo-Weissenberg (Wi^*), and Capillary numbers (Ca_i), [190, 203] defined as

$$Re = \frac{\rho N' D^2}{\eta} \sim \frac{\rho N'^{2-n} D^2}{\eta_0 k^{n-1}} \quad (5.16)$$

$$De^* = \lambda_c N \quad (5.17)$$

$$Wi^* = \lambda_c \dot{\gamma} \quad (5.18)$$

$$Ca_i = \frac{\eta_{i,0} N' D}{\sigma} \quad (5.19)$$

Here, k is a constant dependent only on the geometry of the impeller, σ is the interfacial tension between the polymers, and i is the phase. Re represents the ratio of inertial to viscous forces and characterizes the flow regime. De^* compares the material relaxation timescale to the characteristic process timescale, indicating the degree to which elastic effects persist during flow. Wi^* is the scaled relaxation time using the shear rate and is used to assess the influence of viscoelasticity on shear thinning flow behavior. While De ($De = \lambda N$) and Wi ($Wi = \lambda \dot{\gamma}$) are generally based on a microscopically defined relaxation time, λ , ‘real’ polymers have a spectrum of these relaxation time even for fixed shear-rate. Therefore, to define all viscoelastic effects in this work for computational convenience, we use only one, λ_c to give approximate

qualitative trends rather than quantitative description. Given we are already assuming surrogate polymers with minimal elastic and memory effects, this is a reasonable approximation. Thus, the reported De^* and Wi^* will be overestimated compared to expected values for polymers. Ca_i represents the ratio of viscous forces to interfacial tension forces and governs droplet deformation and breakup in multiphase systems.

We compared impeller performance using mixing time, cavern volume percentage, and specific interfacial area. Mixing time is defined as the time at which all four probes reach 95% of the steady-state tracer concentration.[189] Cavern volume percentage represents the fraction of polymer volume moving faster than 1% of the characteristic impeller speed ($2\pi ND$).[204] The specific interfacial area ($a_{v,d}$) is defined as the surrogate polymer–polymer interfacial area per unit dispersed-phase volume.[205]

5.4 Results and discussion

5.4.1 Temperature and shear rate-dependent viscosity

The experimentally measured viscosities and corresponding Carreau-Arrhenius model fits for LDPE and HDPE (Figure 5.2) are in excellent agreement across all temperatures and shear rates, with a mean absolute percentage error (MAPE) of 4.2% and 5.8%, respectively. These results confirm that the developed Carreau-Arrhenius framework can serve as a reliable predictive tool for estimating polymer melt viscosity under inelastic reactor conditions. The PTT model fit is reported in Figure D.1.

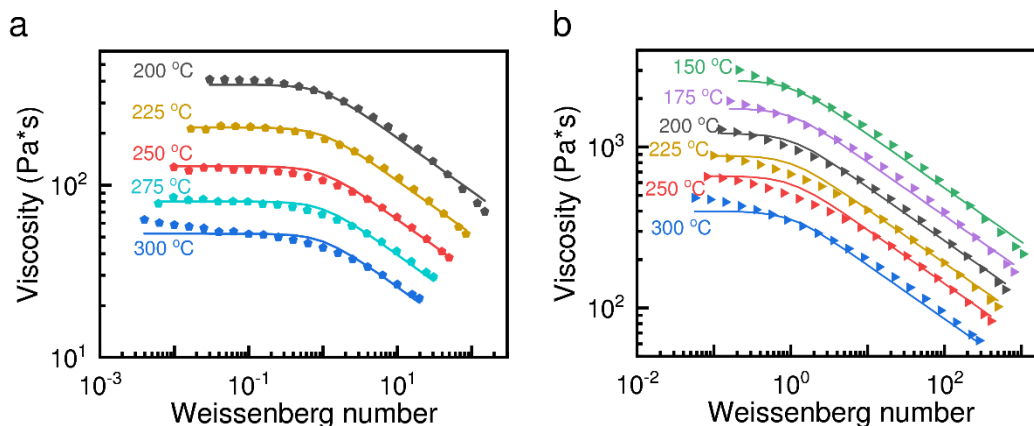


Figure 5.2: Rheological data and model fits using the parameters in Table 5.1. Steady shear viscosity of (a) LDPE and (b) HDPE vs. Weissenberg number for shear rate (0.1 – 500 1/s) across temperatures (150 – 300 °C). Symbols denote experimental measurements, and solid lines show the global Arrhenius fit.

While the fitted model cannot capture the elastic and memory effects, Arrhenius parameters (Table 1) were used to provide molecular-level insight into the structural differences of the two polyethylene samples. The higher flow activation

energies (E_λ and E_{η_0}) of LDPE reflect its long-chain branching, which introduces additional relaxation processes and higher activation barriers for viscous flow.[197, 206] Also, despite LDPE's higher weight-average molar mass ($M_w \sim 71$ kg/mol) than HDPE ($M_w \sim 60$ kg/mol), LDPE exhibited a lower zero-shear viscosity at similar temperatures. This result is corroborated by literature, which attributes this behavior to reduced entanglement density in LDPE due to more chain branching.[207] Thereafter, the developed Carreau model was used to predict the viscosity of the surrogate polymers (P_{LD} and P_{HD}). The predicted values of λ_c and η_0 at 200 °C and 300 °C for the surrogate polymers used in this study are reported in Table 5.2.

Table 5.1: Fitted Arrhenius parameters for LDPE and HDPE.

	A_{η_0} (Pa*s)	E_{η_0} (K)	A_λ (s)	E_λ (K)	n
LDPE	4.25×10^{-3}	5397.6	2.79×10^{-6}	5481.0	0.69
HDPE	2.03	3026.1	1.36×10^{-2}	2134.0	0.66

Table 5.2: Predicted values of Carreau timescale and zero-shear viscosity for P_{LD} and P_{HD} using fitted Arrhenius parameters.

	200 °C		300 °C	
	λ_c (s)	η_0 (Pa*s)	λ_c (s)	η_0 (Pa*s)
P_{LD}	0.3	382.6	0.04	52.3
P_{HD}	1216.4	1.24	0.56	398.5

5.4.2 Viscoelastic non-Newtonian melts

First, we examined the influence of viscoelastic effects on the surrogate polymer melt flow. Polymer melts exhibit both shear-thinning and elastic behavior,

and the relative importance of elastic stresses is typically characterized by Wi , which represents the ratio of elastic to viscous stresses. When Wi approaches or exceeds unity, elastic stresses can significantly alter flow structure and lead to flow instabilities. Here, we report Wi^* (an overestimates of Wi) to give key qualitative insights.

Figure 5.3 illustrates the flow behavior of P_{LD} in a simplified coaxial-cylinder configuration used to investigate viscoelastic effects. The steady-state velocity field (Figure 5.3a,c) shows the expected shear rate-dominated flow, with the highest velocities occurring near the rotating inner boundary and decaying radially outward toward the stationary wall. In contrast, the corresponding Wi^* distribution (Figure 5.3b,d) highlights regions of high shear-thinning behavior. Also, as $Wi^* \gg 1$, elastic stress is dominant. The highest Wi^* values occur near the curved boundaries where shear rates are largest, indicating that shear rates and elastic stresses are strongly localized in these regions. High Wi^* also indicates polymer stretching, which imposes physical resistance to shaft rotation.

These localized elastic stresses can modify flow patterns by introducing additional normal stresses. As a result, regions of high Wi^* may exhibit altered circulation patterns or reduced effective mixing compared with purely viscous shear-thinning fluids.[208] Such effects become increasingly important as viscosity increases or λ_c becomes larger, conditions that are typical for highly entangled polymer melts.[190] Figure D.2a-b illustrates that, under identical operating conditions, the Carreau-Yasuda model fails to capture the observed non-uniformity and asymmetry in high-shear regions, which are resolved when using the viscoelastic PTT model. The disparity between the results of Carreau-Yasuda and PTT model

highlights the importance of incorporating elastic effects to accurately describe heterogeneous mixing behavior. These effects can also impose mechanical constraints on motors and the design of various connection components of the system, such as the shaft and rotors. Additionally, at elevated Wi , viscoelastic stresses may lead to flow instabilities and mechanically induced chain scission, linking viscous dissipation to polymer degradation. While such effects are not considered in the present framework, they warrant careful consideration when operating at high-shear conditions in real systems.

To further illustrate the implications for multiphase systems, Figure 5.3e shows the implications of viscoelastic stresses for multiphase surrogate polymer systems by presenting the evolution of the P_{LD} - P_{HD} interface during mixing. At $t = 0$, P_{HD} is below the interface due to its higher density. As the flow develops, the interface deforms and migrates upward along the rotating cylinder. This behavior is characteristic of viscoelastic fluids and is commonly referred to as rod climbing. In such systems, elastic normal stresses drive the viscoelastic fluid toward regions of higher shear near the rotating shaft. Because P_{HD} exhibits a larger λ_c in comparison to P_{LD} , P_{HD} experiences stronger elastic effects, leading to preferential migration toward the shaft and away from the cylinder wall. In practical reactors, this phenomenon can cause polymer to climb along the shaft and splash on vessel walls. Such redistribution of material can leave portions of the melt poorly contacted with the catalyst, potentially reducing achievable conversion and introducing bias in experimentally measured product distribution.

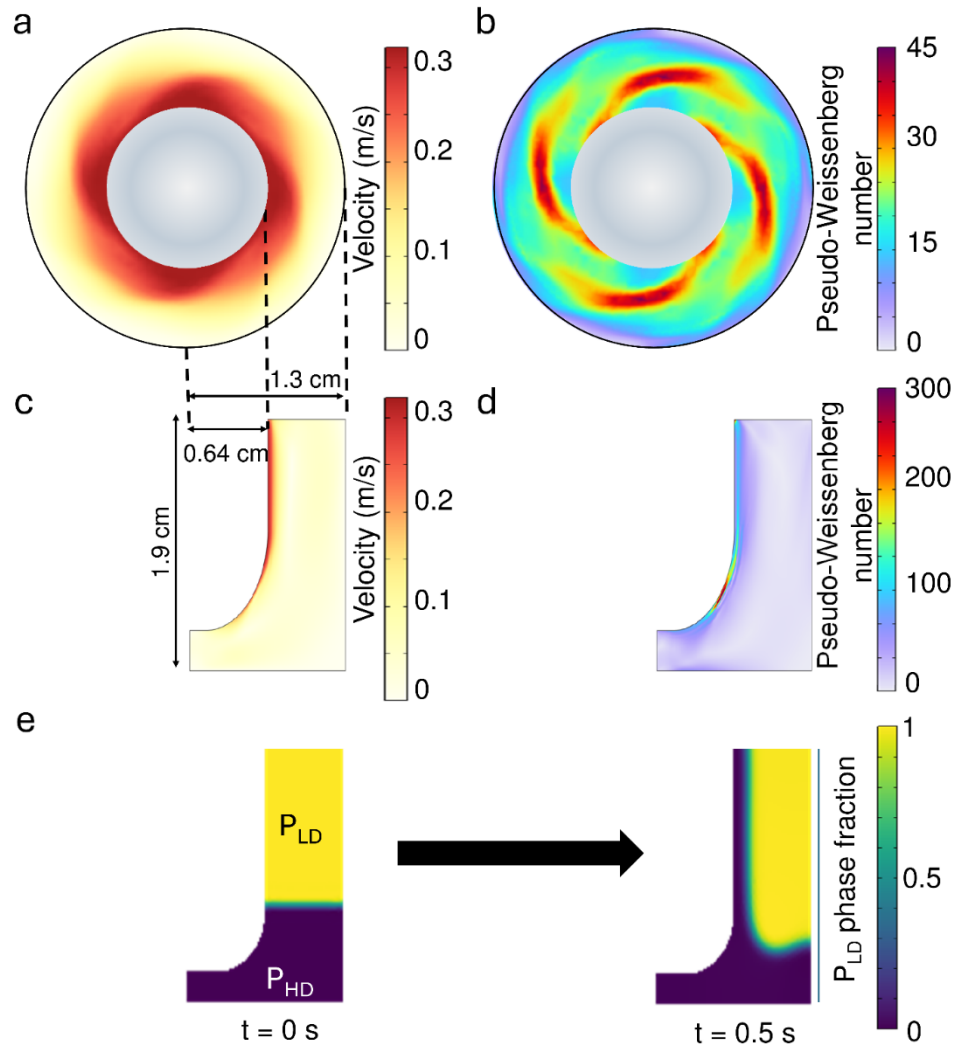


Figure 5.3: Viscoelastic non-Newtonian melt mixing in a 2D coaxial cylinder configuration. The inner rotating cylinder (diameter = 1.28 cm) is enclosed within a stationary vessel (diameter = 2.6 cm and height 1.9 cm). Top-view steady-state flow fields for P_{LD} showing (a) the velocity magnitude and (b) the pseudo-Weissenberg number. Side-view steady-state fields showing (c) the velocity magnitude and (d) the pseudo-Weissenberg number. (e) Evolution of P_{LD} phase fraction during P_{LD} - P_{HD} mixing ($P_{LD}:P_{HD} = 10:1$ vol/vol), showing the interface position at $t = 0$ s and $t = 0.5$ s. $\mu_s = 0.2\eta_0$, $\alpha_e = 0.1$ isothermal domain with $T = 200$ °C, $N = 500$ rev/min. Material properties: P_{LD} ($\eta_0 = 383$ Pa * s, $\lambda_c = 0.3$ s, $\rho = 750$ kg/m³), P_{HD} ($\eta_0 = 1216$ Pa * s, $\lambda_c = 1.24$ s, $\rho = 770$ kg/m³), and $\sigma = 0.87$ mN/m.[55]

To limit elastic redistribution of material, it is necessary to identify operating conditions where elastic stresses remain moderate and viscous transport dominates the flow. A commonly used dimensionless group is De , which compares λ to the deformation time scale imposed by mixing. Generally, the deformation time scale is assumed to be equal to $1/N$ in a mixing vessel. Extensive studies have shown that viscoelastic flow instabilities and elastic-driven secondary flows become pronounced when $De \geq 1$, whereas flows remain predominantly viscous when $De < 1$. [55, 190] Figure D.2c and D.2d compare the shear-rate distributions predicted by the PTT and Carreau-Yasuda models, respectively, under conditions wherein $De^* < 1$. While the PTT model exhibits some localized asymmetric shear regions, these features remain well homogenized with the surrounding flow and closely align with the predictions of the Carreau-Yasuda model. This agreement supports the use of the Carreau-Yasuda model for our surrogate polymers under conditions where elastic effects are weak.

In a general lab-scale set-up, the rotational speed is fixed due to the experimental protocol (~ 500 rev/min), leaving temperature as the primary variable that can reduce viscoelastic effects by decreasing the λ_c of the polymer melt. While increasing temperature can decrease λ_c , we cannot go beyond the degradation point. Also, increasing temperature increases the intrinsic catalytic kinetic rates requiring faster mass transfer to avoid operating in a transport-limited regime. These results highlight the need to carefully select operating temperatures that balance catalytic activity with viscoelastic behavior when designing and scaling reactors for polymer processing. It is important to do multi-mode modeling to capture the exact temperature and impeller rotational speed, which will indeed capture the operating conditions that will ensure $De < 1$. However, as capturing multi-mode relaxation behavior is out of

scope for this work, the subsequent analysis focused on operating conditions assuming $De^* < 1$ for P_{LD} . This condition allows stable flow fields and meaningful comparison of impeller hydrodynamics, and enables the utilization of the Carreau-Arrhenius model to predict apparent viscosity. Although $De^* < 1$ might not be achievable in multi-surrogate polymer melts, we use the Carreau model to minimize computational time and to qualitatively elucidate several key trends, which can assist impeller design and improve transport.

5.4.3 Model validation and comparison of impellers

To validate our 3D CFD model, power-consumption experiments were performed using a two-blade anchor impeller at 300 °C. Owing to the small melt volume considered here, rotation induced appreciable deformation of the polymer-air interface. To preserve a nominal 2 g effective working volume and maintain a stable free surface, Δm was included in the experiments. Using the experimentally observed convex interface shape, this excess mass was estimated to be approximately 3 g (Section D.1). We acknowledge that the addition of extra mass can alter thermal and mass transport by increasing resistance within the system. However, for the fixed working volume investigated here, the resulting trends are expected to remain qualitatively consistent between experiments and simulations. Under these assumptions, Figure 5.4a shows good agreement between the CFD-predicted and experimentally measured power requirements.

At lower rotational speeds, the required power in experiments is lower than CFD predicted values. This deviation is attributed to the relatively small absolute power demand in this regime, where frictional and mechanical losses are comparable to the measured torque and are difficult to fully account for experimentally. As the

rotational speed is increased, the agreement between simulations and experiments improves. The observed deviation is also attributed to the use of surrogate polymer models, while the experiments employ real LDPE. Incorporating multi-mode viscoelastic models to capture the full relaxation spectrum is expected to improve quantitative agreement.

At higher speeds, experimental deformation of the polymer-air interface led to an increase in the steady-state melt height and spillage on the reactor wall, effectively redistributing the polymer mass and reducing the fraction of the melt that interacted directly with the impeller. Also, due to the rod-climbing nature of LDPE (despite being minimized by operating at a high temperature), we observe mass accumulated over the shaft. The amount of mass accumulated is relatively very small compared to the total mass of the polymer inside the vessel. As a result, the experimentally measured power is lower than that predicted by the CFD model, which assumes a constant mixing volume and a fixed free surface. This behavior is consistent with experimental observations of surface deformation at elevated rotational speeds.[53] Improved agreement could be achieved by incorporating a dynamic free-surface model that accounts for interface deformation and uses the exact polymer mass distribution observed experimentally.

Figure 5.4b presents the CFD predicted power required to achieve a given rotational speed for different impeller configurations. While the magnetic stirrer exhibits the lowest power requirement, its practical applicability is limited by the difficulty in delivering higher torque through magnetic coupling. In contrast, anchor impellers require higher power but are directly driven by motors, making these power levels readily achievable in practice. Furthermore, all anchor configurations exhibit

comparable power requirements, as they generate similar shear distributions within the reactor. A dimensionless group used for scale-up is the product of dimensionless power and the Reynolds number, $N_p \times Re$. The CFD predicted value of $N_p \times Re$ for an anchor impeller is consistent with geometry-dependent empirical correlations reported in the literature (51.4),[57] supporting the validity of the model. The value of $N_p \times Re$ increases with the number of impeller arms and with the addition of a secondary turbine, reflecting increased hydrodynamic resistance and energy dissipation for these configurations. The magnetic stirrer exhibits the highest $N_p \times Re$ value among the systems studied, indicating lower hydrodynamic efficiency and a higher energy requirement to achieve comparable flow intensity. Importantly, $N_p \times Re$ serves as a key scaling parameter for generalized Newtonian mixing systems, linking power consumption to flow intensity across reactor sizes. For scale-up, maintaining a constant $N_p \times Re$ ensures that the ratio of viscous dissipation to flow circulation remains similar, thereby preserving shear distribution and mixing characteristics. $N_p \times Re$ enables estimation of the required power input and impeller speed at larger scales from laboratory data, providing a practical basis for scale-up in viscous, generalizable Newtonian systems where the conventional Re similarity cannot be achieved.

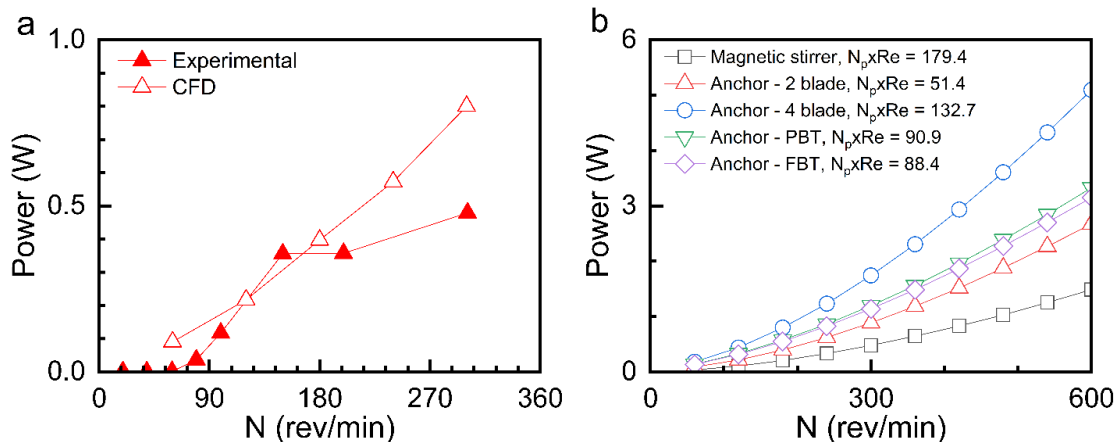


Figure 5.4: Total power required for impeller rotation at a given rotational speed. (a) Experimental and CFD-predicted power requirements for the two-blade anchor impeller in a vessel containing a nominal 2 g of LDPE (P_{LD} for CFD) melt at 300 °C and $\Delta m = 3$ g. (b) CFD predicted power requirement by all impellers at 300 °C. The legend also reports the corresponding value of $N_p \times Re$, which is an important dimensionless number used to scale-up impellers.

5.4.4 Single-phase impeller performance

We use the validated model to compare the performance of the magnetic stirrer and anchor impeller. Figure 5.5a(i) and b(i) shows the steady-state dimensionless temperature (T/T_{wall}) as a function of N_p and Re . For creeping-flow conditions ($Re < 1$), N_p is primarily governed by N ($1/N^3$), followed by the total power delivered to the shaft (P_{tot}), indicating that the required power increases strongly with impeller speed. In contrast, Re increases linearly with N . As a result, increasing impeller speed shifts the system toward higher Re but much lower N_p .

To achieve a nominal rotational speed of $N \sim 500$ rev/min, which is commonly employed in lab-scale catalytic studies, the 3D CFD model predicted that a magnetic

stirrer requires $P_{tot} \sim 1\text{-}4\text{ W}$ and a corresponding torque (τ) on the order of $10^{-2}\text{-}10^{-3}\text{ N}\cdot\text{m}$ when T_{wall} is $300\text{ }^{\circ}\text{C}$. However, typical laboratory magnetic stirrers are rated at $\sim 3\text{ W}$ motor output. For lower wall temperatures ($T_{wall} < 250\text{ }^{\circ}\text{C}$), at which melt viscosity is significantly higher, the required torque exceeds the motor capacity, limiting the attainable rotational speed and potentially leading to mixing-limited operation. In contrast, anchor impellers require slightly higher power ($\sim 2\text{-}8\text{ W}$) but are directly motor-driven, making these operating conditions practically attainable. For the same N range, the anchor impeller exhibited lower N_p values than the magnetic stirrer, suggesting reduced effective power demand (Figure 5.5a(i) and 5.5b(i)). This behavior is primarily attributed to the larger impeller diameter of the anchor configuration, which lowers the N_p , as well as shear-thinning-induced viscosity reduction at high local shear rates.

These differences in power delivery directly influence mixing behavior. The anchor impeller generates higher shear rates near the blades, reducing local viscosity and promoting stronger circulation, as evidenced by the velocity and viscosity fields (Figure 5.5iii-iv). This shear-induced viscosity reduction enhances bulk transport and minimizes stagnant regions. In contrast, the magnetic stirrer produces weaker circulation, resulting in slower mixing and reduced effective interaction between fluid regions. Similar trends observed across all anchor configurations confirm that close-clearance designs improve mixing efficiency in highly viscous systems (Figure D.3).

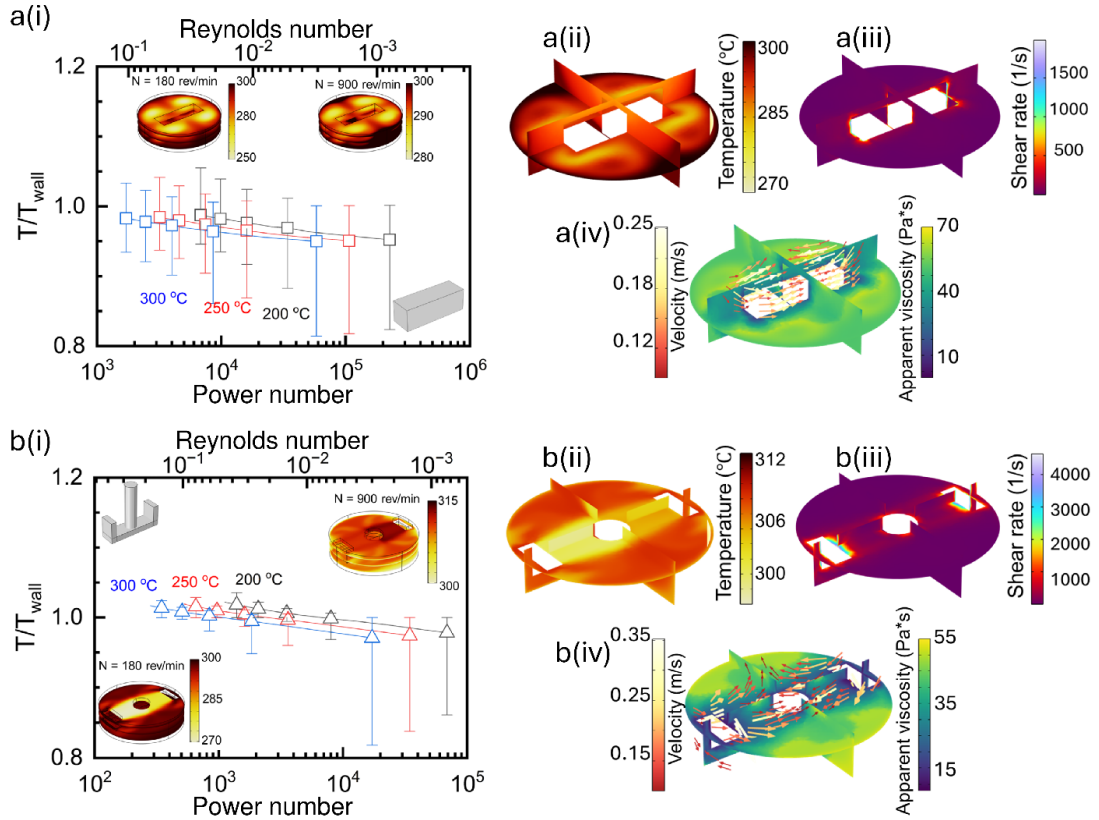


Figure 5.5: Performance of 3D (a) magnetic stirrer and (b) anchor impeller for 2 g of P_{LD} . (i) Dimensionless temperature vs. N_p and Re ($N = 60$ -900 rev/min). The symbols are the average volume temperatures, and variability bars show the minimum and maximum inside the domain. The insets show the temperature profiles when T_{wall} is 300 °C and $N = 180$ rev/min or 900 rev/min. (ii) Temperature, (iii) shear rate, and (iv) dynamic viscosity and velocity profiles. T_{wall} is 300 °C and $N = 420$ rev/min.

The impact of these hydrodynamic differences is most evident in the temperature field. The magnetic stirrer exhibits substantial thermal gradients, with hot regions near the vessel walls and temperature differences of up to approximately 60 °C across the domain, indicating poor heat transfer and limited bulk mixing. These effects are expected to be even more pronounced for higher-viscosity systems, which

would result in increased torque demand, stronger viscous dissipation, and more pronounced thermal gradients. In contrast, the anchor impeller achieves near-isothermal conditions over a broad operating range. At moderate N_p ($\sim 10^3$), the average temperature approaches T_{wall} , while at lower N_p it slightly exceeded T_{wall} due to localized viscous dissipation. Moreover, the temperature difference between the maximum and minimum values became negligible, indicating near-isothermal operation for $N_p \cong < 10^3$ ($P_{tot} \sim 0.5\text{-}2$ W, $N \sim 400\text{-}500$ rev/min). This reflects efficient heat transport enabled by strong radial-axial circulation and wall-scraping action. Spatial temperature profiles (Figure 5.5ii) further confirm that anchor impellers eliminate hot spots near the vessel walls, unlike magnetic stirrers. These characteristics make the anchor impeller more suitable for lab-scale catalytic studies, as it ensures consistent transport conditions across temperatures. Even as viscosity changes with temperature, the anchor geometry's enhanced mixing and wall-scraping action will maintain temperature uniformity and reduce stagnant zones. To further quantify this behavior, we also report the coefficient of variation for temperature as a function of N for the anchor impeller in the Appendix D (Figure D.4).

This temperature gradient has important implications for catalytic performance comparisons across temperatures. Because melt viscosity is strongly temperature-dependent, operating at nominally identical stirrer settings with temperature gradients does not guarantee identical mixing intensity, heat transfer rates, or cavern formation. Consequently, variations in mixing across operating temperatures may influence the observed reaction environment, complicating direct comparisons of catalytic performance. Due to the general high density of the catalyst, it might be localized, causing non-uniform reaction rates across the volume. Moreover, the elasticity of real

polymers would increase the local elastic stress tensor resulting in an increase in local viscous heat dissipation. Due to higher heat being produced for the same thermal dissipation, real polymers may exhibit greater thermal gradients versus the surrogate polymer used in this work.

While the spatial temperature, shear rate, velocity, and viscosity profiles provide qualitative insights into mixing, we also evaluated quantitative metrics, including the mixing time and cavern volume (Figure 5.6). The mixing time was calculated using a passive pseudo-tracer introduced in the surrogate polymer melt to track concentration homogenization within the domain. Figure 5.6a illustrates the surrogate polymer melt domain, showing the tracer injection location and probe positions used to monitor concentration evolution. The probe concentration profiles indicate that the tracer gradually converge to a uniform steady-state value, confirming bulk homogenization.

Figure 5.6b presents the mixing time as a function of N_p for all the impellers studied. For a rotational speed of $N = 500$ rev/min, the magnetic stirrer requires approximately 1 W of power and achieves a mixing time of ~ 15 s. In contrast, the two-blade anchor impeller operates at comparable power input but reduces the mixing time to ~ 3 s, representing nearly a fivefold improvement in mixing efficiency. This performance advantage persists across the entire range of rotational speeds investigated, demonstrating the superior circulation of anchor geometry. The only exception is the four-blade anchor impeller, which exhibited a longer mixing time relative to the two-blade design. The additional blades increase radial displacement of the melt but reduce effective axial circulation, leading to less efficient bulk homogenization. These results highlight that increasing blade count does not

necessarily improve mixing performance in highly viscous, creeping-flow systems; rather, impeller geometry must balance radial and tangential flow components to maximize circulation efficiency.

Although the predicted mixing times are in the order of seconds to minutes, much shorter than typical batch reaction times, impeller geometry remains critical for reactor performance. Mixing time reflects the rate of bulk homogenization of a tracer and is representative of bulk circulation and stagnant regions, but it does not fully capture the spatial structure of the flow field. These differences are further clarified through cavern volume analysis.

Cavern volume percentage represents the fraction of the surrogate polymer melt that actively circulates during mixing and is defined as the portion of the reactor volume moving faster than 1% of the characteristic impeller tip speed. Figure 5.6b shows that anchor-type impellers produce cavern volumes exceeding 90% of the total melt volume, indicating that nearly the entire reactor contents participate in active circulation. In contrast, systems with weaker bulk circulation can develop localized stagnant regions where fluid velocities fall below this threshold. Because catalyst particles generally follow melt streamlines, cavern volume provides a hydrodynamic measure of the region effectively accessible for reaction. Reduced active volume increases the likelihood of localized temperature gradients and uneven catalyst exposure, which can influence apparent reaction rates even when bulk mixing appears to be rapid.

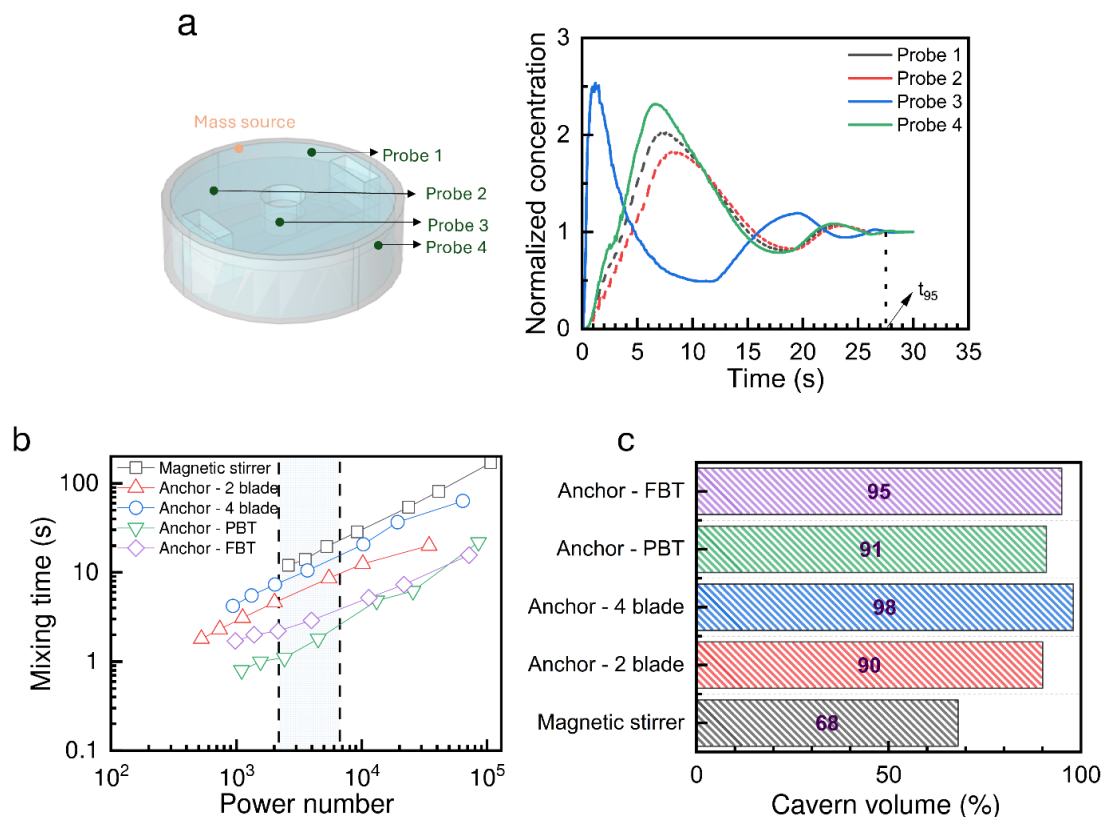


Figure 5.6: Mixing performance across various impellers. (a) Normalized concentration vs. time at by four probe locations within the reactor volume (two-blade anchor impeller, P_{LD} , $N = 60$ rev/min, $T_{wall} = 300$ °C). Probe coordinates are $(-0.37, 0.37, 0.40)$ cm, $(0.58, -0.58, 0.20)$ cm, $(-1.10, 0.53, 0.23)$ cm, and $(0.53, -1.10, 0.30)$ cm. The origin, $(0, 0, 0)$, corresponds to the bottom center of the vessel. (b) Mixing time vs. N_p ($N = 60$ -900 rev/min). The shaded region represents the typical lab operating regime. (c) Cavern volume percentage for each impeller.

During catalytic reactions, the formation of lower-molecular-weight liquid products may reduce melt viscosity over time. Therefore, dependent on the reaction timescale, the system will behave differently. When the reaction timescale is comparable to or shorter than the mixing timescale, viscosity evolution during reaction can reduce the absolute mixing time. However, when the reaction timescale is

significantly longer than the mixing timescale, as is typically the case with polymer chemistries, the melt is expected to remain effectively well mixed, with negligible bulk concentration gradients after the initial homogenization stage. Therefore, the relative performance differences between impeller geometries are governed primarily by flow topology and wall interaction, which remain controlled by impeller design. Thus, while viscosity evolution may improve overall mixing rates, the superiority of configurations in maintaining high active volume and thermal uniformity is expected to persist.

5.4.5 Two-phase (immiscible polymers) impeller performance

While LDPE constitutes a major fraction of plastic waste, it is commonly encountered with other polymers, such as HDPE and polypropylene (PP), in mixed plastic waste streams and MLFs. Because HDPE and PP are generally immiscible with LDPE, they can form complex multiphase systems during processing. Therefore, it is essential to analyze such multi-component mixtures to understand the mixing and interfacial phenomena governing catalytic conversion. It should be noted, however, that post-consumer polyolefin waste often has higher molecular weight, higher degree of entanglement, and a broader spectrum of relaxation times than the surrogate polymers used here. These differences may affect the quantitative values reported below, but the simulations provide useful qualitative trends for understanding how viscosity differences, interfacial tension, and impeller design influence multiphase polymer-melt mixing. To this end, we modeled a pseudo-binary PLD-PHD system that acts as mixed plastic surrogate, with PLD as the continuous phase and PHD (the denser polymer) initialized at the bottom at $t = 0$. Based on our earlier findings that anchor impellers produce nearly isothermal flow fields, we assumed isothermal

conditions here to minimize computational cost. The results are reported at steady state, defined as the time beyond which the interface shows no further observable evolution. The steady state was found to be after 5 revolutions of the impeller (Figure S5). Very few revolutions are required because we are not considering viscoelastic effects in 3D two-phase CFD simulations.

Figure 5.7a shows that the specific interfacial area is highly sensitive to N_p . Initially, decreasing N_p (increasing N) reduces $a_{v,d}$ due to enhanced macro-coalescence, where larger dispersed domains merge into even larger structures,[11] reducing the total interfacial area. Beyond a critical N_p (1.1×10^3), microdispersion dominates, in which increased shear breaks larger domains into smaller droplets,[58] reducing the total interfacial area. Beyond a critical N_p (1.1×10^3), microdispersion dominates, in which increased shear breaks larger domains into smaller droplets,[58] increasing $a_{v,d}$. Both the average and maximum velocities within the dispersed phase rise with increasing N , highlighting the importance of operating at high impeller speeds to maximize the interfacial area. Increased interfacial area directly improves mass transfer between immiscible surrogate polymer phases, which is critical in catalytic systems wherein reactants, intermediates, or active catalytic sites may be distributed across phases. Enhanced mass transfer reduces diffusion limitations, promotes more uniform reactant availability, and can lead to improved catalyst utilization and more consistent reaction environments across the reactor.

To generalize these observations, we conducted a parametric analysis in the dimensionless design space defined by the Capillary number of the continuous phase (Ca_c) and the viscosity ratio of dispersed and continuous phases ($\frac{\mu_d}{\mu_c}$), where c and d are the indices of the continuous and dispersed phase, respectively. Ca_c quantifies the

balance between viscous and interfacial forces, where viscous stresses are governed by the continuous phase and interfacial tension is modifiable using surfactants. As shown in Figure 5.7b, a lower Ca_c value increased $a_{v,d}$ when the dispersed phase is more viscous, since coalescence dominates under these conditions. Thus, enhancing dispersion by increasing interfacial tension (i.e., reducing Ca_c) is advantageous. Conversely, when the continuous phase is more viscous, adding surfactants (increasing Ca_c) enhances $a_{v,d}$ (Figure 5.7c). As surfactant tuning is experimentally feasible, these findings indicate that having the higher-viscosity polymer as the continuous phase provides superior control over mixing and dispersion. This conclusion is also supported by Figure 5.7d wherein a lower ratio of viscosities indicates a higher $a_{v,d}$. Figure 5.7d also indicates that a moderate ratio is optimal; the data show a moderate increase in $a_{v,d}$ with an increase in viscosity ratios for lower values of viscosity ratios, while $a_{v,d}$ significantly drops with an increase in viscosity ratios for higher viscosity ratios.

Finally, Figure D.6 maps $a_{v,d}$ across the full design space, showing a highly nonlinear response surface with multiple local optima. This complexity combined with high computational cost underscores the need for systematic mapping of the design space and motivates the development of physics-informed guidelines to identify high-performance operating regimes for reactor and impeller design.

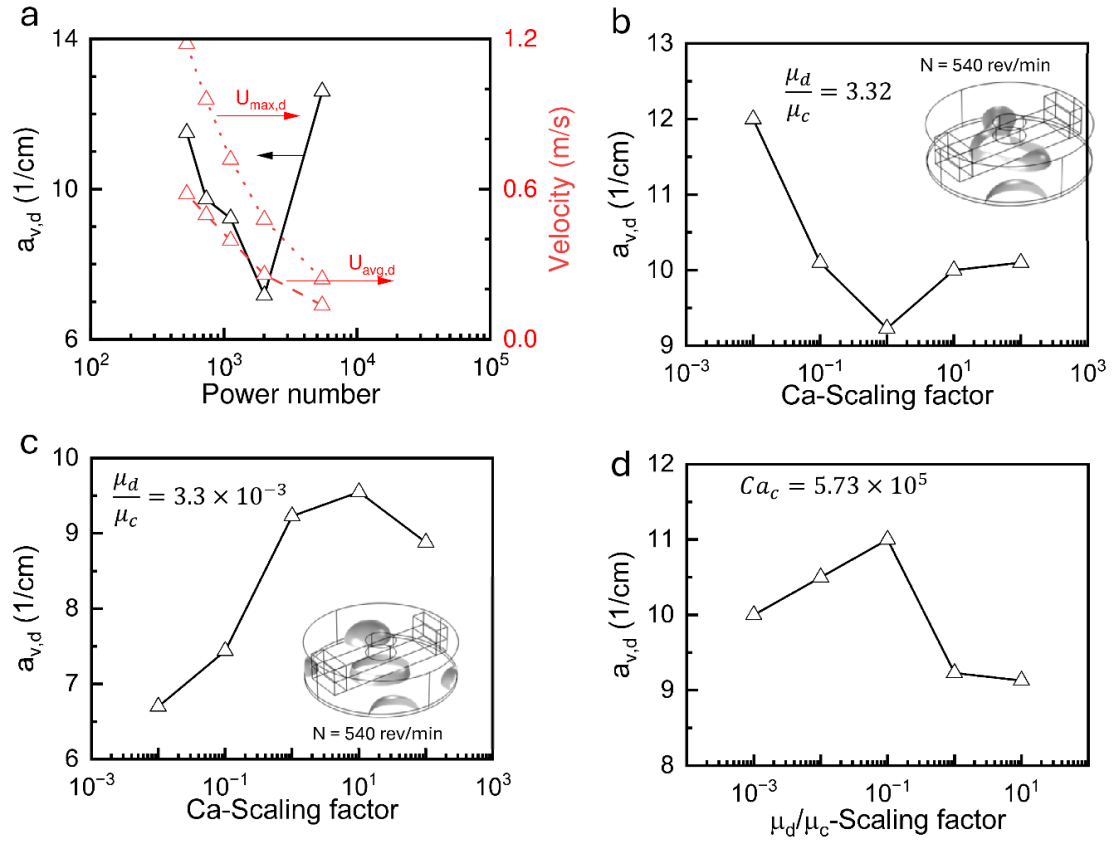


Figure 5.7: Surrogate multi-polymer mixing performance using a two-blade anchor impeller (P_{LD} : P_{HD} (v:v) = 10:1, $T_{wall} = 300$ °C). (a) Specific interfacial area, and average and maximum speed within the dispersed phase ($N = 180$ -900 rev/min). (b) Specific interfacial area vs. Ca-scaling factor ($N = 540$ rev/min, $\frac{\mu_d}{\mu_c} = 3.32$). The inset shows the surrogate polymer-polymer interface ($N = 540$ rev/min, $\frac{\mu_d}{\mu_c} = 3.32$, $Ca_c = 5.73 \times 10^5$), with P_{HD} in the volume outlined by the grey surface and P_{LD} in the surrounding phase. (c) Specific interfacial area vs. Ca-scaling factor ($N = 540$ rev/min, $\frac{\mu_d}{\mu_c} = 3.3 \times 10^{-3}$). The inset shows the polymer-polymer interface ($N = 540$ rev/min, $\frac{\mu_d}{\mu_c} = 3.3 \times 10^{-3}$, $Ca_c = 5.73 \times 10^5$), with P_{HD} in the volume outlined by the grey surface and P_{LD} in the surrounding phase. (d) Specific interfacial area vs. $\frac{\mu_d}{\mu_c}$ -scaling factor ($N = 540$ rev/min, $Ca_c = 5.73 \times 10^5$).

While the anchor impeller provides excellent baseline mixing, its ability to further enhance dispersion is limited. To improve phase breakup and interfacial renewal, we employed coaxial impellers that combine an anchor with either FBT or PBT. Figure 5.8a shows the polymer-polymer interface patterns for these configurations, revealing visibly improved macro-dispersion upon turbine integration. Quantitative analysis Figure 5.8b indicates that the anchor + FBT configuration increases $a_{v,d}$ by nearly fourfold compared to the anchor alone, for the same input power—translating to enhanced mass-transfer efficiency and improved catalyst utilization.

Given its superior performance, we conducted a parametric study on the anchor + FBT system (Figure 5.8c-d). The results show that performance is highly sensitive to the turbine diameter, but only marginally affected by the turbine height. Turbines with diameters comparable to the anchor width and moderate heights yield optimal interfacial area and energy efficiency, making them ideal for multi-polymer melt mixing and catalytic applications. Unlike the surrogate system modeled here, experimental HDPE and LDPE may phase separate, leading to the formation of HDPE-rich and HDPE-poor regions. The present CFD simulations primarily resolve the P_{HD} -rich phase due to limitations in mesh resolution. Capturing finer-scale, P_{HD} -poor domains would require significantly higher mesh refinement, which would substantially increase the computational cost.

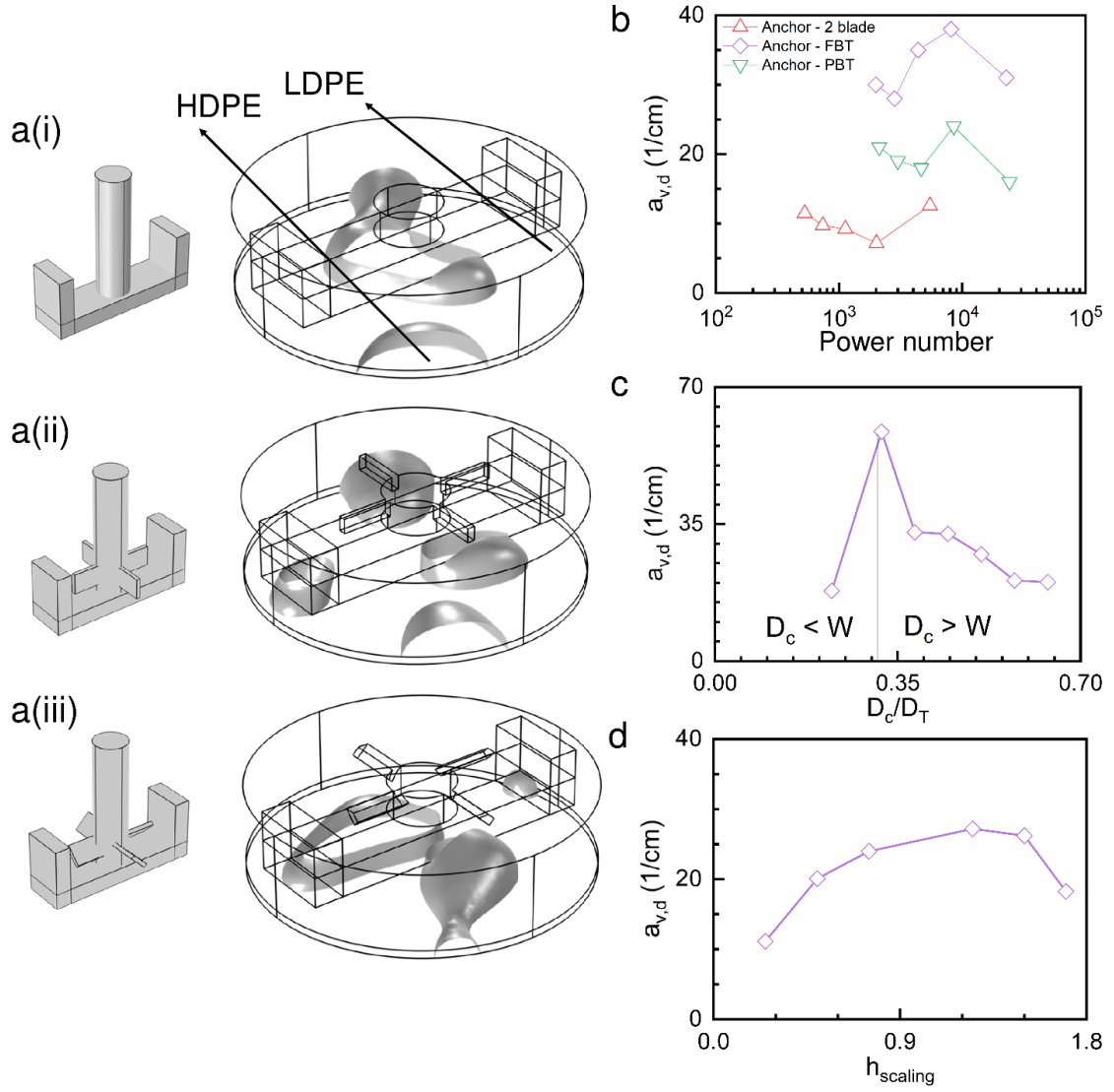


Figure 5.8: Impeller performance for multi-polymer mixing. (a) LDPE and HDPE interface using (i) anchor impeller, anchor impeller + flat blade turbine, and (iii) anchor impeller + pitched blade turbine at steady state, with HDPE in the volume outlined by the grey surface and LDPE in the surrounding phase. (b) Specific interfacial area obtained using impellers ($N = 180\text{-}900$ rev/min) with dimensions mentioned in Figure 5.1. (c) Impact of change of D_c on specific interfacial area while keeping D_T constant (D_c = Axial impeller diameter, D_T = Tank diameter = 2.54 cm, W = width of anchor impeller). (d) Impact of change of h on specific interfacial area (h = distance between turbine and bottom of the tank, h_i = nominal value of $h = 0.16$ cm, $h_{\text{scaling}} = h/h_i$).

5.5 Conclusion

In this work, we developed a comprehensive reactor-scale framework to understand and design mixing and heat transfer in highly viscous, generalizable Newtonian fluids, under conditions where the dominant non-Newtonian rheological effects can be approximated as shear- and temperature- dependent viscosity. By integrating rheological characterization, constitutive modeling, CFD simulations, and experimental validation, we established a first step toward quantifying the interplay between viscosity, viscoelasticity, and impeller hydrodynamics in small-scale batch reactors commonly used for catalytic hydroconversion studies. When $De^* < 1$, the Carreau-Arrhenius model provides an effective, computationally-efficient, and accurate framework for reactor-scale simulations. Importantly, using surrogate polymer melts, we demonstrated that shear rate-dependent rheology can be used to directly estimate motor power and torque requirements, enabling rational design of mixing systems without extensive trial-and-error experimentation.

A key finding of this work is the identification of critical limitations of magnetic stir bars for polymer melt processing. Despite their widespread use in laboratory studies, magnetic stirrers are unable to deliver sufficient torque at high viscosities, which results in large thermal gradients across the polymer melt and non-uniform transport conditions. These limitations can complicate the interpretation of catalytic performance, particularly when comparing results across temperatures. In contrast, close-clearance anchor impellers provide superior hydrodynamic behavior, achieving near-isothermal operation, faster mixing, and high cavern volume (>90%), thereby ensuring effective catalyst accessibility and uniform reaction environments. We further show that impeller geometry strongly influences mixing efficiency, and

that increasing blade complexity does not necessarily improve performance in creeping-flow systems.

For our surrogate, immiscible multi-polymer systems, we demonstrate that the interfacial area between the two viscous hydrocarbon melts, and consequently mass transfer, is highly sensitive to operating conditions and viscosity ratios. Coaxial impeller configurations, particularly anchor-flat blade turbine combinations, significantly enhance dispersion and interfacial renewal, providing a pathway to improve catalyst utilization in multiphase systems.

Overall, this work makes first strides to provide practical, experimentally relevant guidelines for selecting impeller configurations, operating conditions, and reactor designs for polymer processing. These insights are expected to facilitate the scale-up of catalytic plastic recycling technologies and further motivate more detailed theoretical/computational and laboratory studies necessary to quantitatively explore a wider range of operating conditions.

Chapter 6

STEAM CRACKING OF PLASTICS-WASTE NAPHTHA THROUGH RETROFITTING

6.1 Contribution

All the work in this chapter is done by thesis' author. This chapter is based on submitted work in Joule.

6.2 Introduction

Plastic waste is increasingly recognized as an environmental liability and mismanaged carbon source, with more than 400 million metric tons produced each year.[209] Global plastics production has risen rapidly over the decades, with most post-consumer plastics still following a linear pathway through landfilling (>75%), incineration (16%), or environmental leakage rather than recycling.[47, 48] Among plastics waste (PW), polyolefins are the largest fraction, but are difficult to separate and mechanically recycle or upcycle at high purity.[210-212] Mixed, contaminated, or degraded polyolefin streams require alternative valorization pathways.[213, 214]

Thermochemical conversion of PW is a promising route. Hydrocracking is especially attractive because it is faster than hydrogenolysis and transforms polyolefins under comparatively mild conditions into paraffins with narrower, more refinery-compatible product distributions than those of pyrolysis.[49, 215] Naphtha is a particularly strategic target because it serves as the principal feedstock for steam crackers and catalytic reformers, thereby connecting PW upgrading directly to existing

olefins and aromatics infrastructure.[25, 29, 216] Recent advances in Ni/BEA catalysts have found that low-density polyethylene (LDPE) can be converted to naphtha at high yield, with a competitive minimum selling price (MSP) and global warming potential (GWP) to conventional naphtha, highlighting a practical opportunity to retrofit the PW hydrocracking product into existing refineries.[49, 52, 217]

Currently, little is known about how to integrate PW naphtha into existing assets. Prior techno-economic analysis (TEA) of PW upcycling technologies consistently shows that commercial viability depends not only on product yield, but also on PW logistics, product slate, separations, utilities, and scale.[52, 218, 219] In particular, PW cost, coproduct value, and separation intensity repeatedly emerge as dominant cost drivers.[27, 51, 60, 220, 221] These findings imply that PW naphtha should not be treated as a simple drop-in replacement for fossil naphtha. Its value depends on how its composition affects steam cracker product selectivity, downstream separation duty, and overall plant economics under existing assets.[12]

This challenge is amplified by the fact that the carbon-number distribution of PW naphtha depends strongly on the catalyst, temperature, residence time, and hydrogen pressure during hydrocracking.[49, 52, 217] As a result, upstream catalyst and process choices impact downstream steam-cracker performance. Recent machine-learning studies have shown that data-driven optimization can accelerate PW-conversion process design by rapidly identifying operating conditions, such as reaction temperature and hydrogen partial pressure, that optimize multiple objectives, including profit and GWP.[27] However, composition-aware optimization of PW naphtha for steam-cracker remains largely unexplored. Importantly, an integrated framework that connects upstream PW hydrocracking, downstream steam cracking, refinery process

constraints, and feedstock collection and sorting economics, in a form that supports real deployment decisions, is missing.

Here we develop such a framework. We couple detailed kinetics simulations, process simulation, TEA, and active learning to evaluate the integration of PW naphtha into industrial steam crackers. Rather than assuming fixed steam cracker product yields or allowing unrestricted process design, we preserve the base-case separation train and assess value creation under realistic retrofit constraints. In this way, the work goes beyond standalone PW analysis and answers deployment-oriented questions. This work addresses compositions, criteria for favorable collection and sorting conditions such as population density, and retrofit strategies that can create measurable economic advantage in existing steam-cracking infrastructure. By linking catalyst-informed feed design to refinery-scale economics, this study establishes a route toward actionable and industrially relevant chemical valorization of polyolefins.

The remainder of this paper is organized as follows. Section 6.3 presents the integrated framework combining retrofit-constrained process simulation, microkinetics, techno-economic analysis, and active learning. Section 6.4 applies this framework to benchmark conventional naphtha cracking, evaluate alternative retrofit strategies for PW naphtha integration, map the role of PW naphtha source on the olefins MSP through population density, and identify an economically favorable PW naphtha composition under industrially relevant conditions. Section 6.5 summarizes the main findings and outlines their implications for deploying PW naphtha as a low-carbon feedstock in existing steam-cracking assets.

6.3 Methods

6.3.1 Aspen Plus Process Simulation

Process simulations were performed using Aspen Plus V12 (Aspen Technology, Inc.). The vapor-liquid equilibrium was described using thermodynamic models appropriate for hydrocarbon and hydrocarbon-water mixtures encountered in naphtha steam cracking. All chemical species properties were selected from the Aspen Plus physical property database. The steam cracking furnace train was modeled using an RStoic reactor block, in which reaction yields were specified with a microkinetic model (Section 6.3.3).[8, 222, 223] The remaining process units, including heat exchangers, compressors, and separation columns, were modeled using standard Aspen Plus unit operation blocks.

To ensure industrial relevance, we adopted a retrofit methodology with the base case of crude oil-derived naphtha steam cracking flowsheet as a reference [62] All scenario-based analyses were conducted by varying operating conditions, specifically the temperature and residence time of the steam cracker, the PW naphtha mass fraction, and the feed to distillate ratio in separation columns, without altering the number of stages or structural configuration of downstream separation units. This constraint assesses the feasibility of integrating PW feeds into existing infrastructure. We also ensured that the separation columns stayed within hydraulic limits, since the total naphtha feed rate was held constant.

6.3.2 Techno-Economic Analysis

The Aspen Process Economic Analyzer V11 was used to determine the capital and operating costs. Equipment sizing and cost estimation were conducted using Aspen's built-in correlations, and all costs are reported in U.S. dollars adjusted to the

reference year of analysis.[224] Discounted cash flow analysis was conducted, and the MSP, defined as the selling price of the product when the net present value is zero, was calculated.[224] Other key economic metrics, including total capital investment (TCI) and total cost of manufacturing (TCM), were also calculated under consistent assumptions. Heat integration was implemented using the Aspen Energy Analyzer. Additional TEA assumptions are presented in Appendix E (Section E.1).

6.3.3 Kinetic model

The microkinetic model used in this study was adopted from prior literature and reformulated in OpenMKM.[155] OpenMKM is a multiphysics, multiscale, open-source software package featuring state-of-the-art C++ solvers. The model includes a comprehensive reaction network comprising 492 chemical species and 17,790 elementary reactions, spanning C₁–C₁₆ hydrocarbons across both low and high temperatures.[222, 223] Model validation of product distributions was performed against the literature, demonstrating good agreement across operating conditions (Table E.1).[62] The validation procedure and assessment are provided in Section E.2. Simulations were conducted in an isothermal, isochoric 0D plug flow reactor (PFR). The resulting steam cracker product yields were then provided to the Aspen Plus process simulation.

6.3.4 Active learning

PW hydrocracking produces a widely varying naphtha composition depending on the catalyst, reaction temperature, residence time, and hydrogen pressure. To efficiently screen the composition space and identify feeds with the greatest downstream economic benefit, the PW naphtha composition was represented by a

normal distribution defined by two independent descriptors: the weighted-average carbon number and its standard deviation. Literature-reported PW naphtha compositions demarcated an average carbon number of 5–12 and a standard deviation of 1.5–5.[61, 215, 217, 218, 225-228] An active-learning framework, shown in Figure 6.1, was used to identify the composition that minimizes olefins' MSP using a minimal number of simulations.

In this framework, an initial design space comprising 10 compositions was generated using Latin hypercube sampling to ensure broad and uniform coverage of the input domain.[229] For each sampled composition, steam cracker product yields were predicted using the microkinetic model at the temperature and residence time identified from the scenario-based analysis, giving the olefins' MSP (Section 6.4.2, scenario 5, Table 6.1). These yields were subsequently employed in individual retrofit-constrained process flowsheets to compute the olefins' MSP. Because variation in feed composition altered the product distribution of the steam cracker, each case required adjustment of downstream operating variables while preserving the retrofit constraint.

Following the initial sampling, an iterative active learning strategy was employed using NEX Torch, an open-source Python/PyTorch-based framework for Bayesian optimization, to build a surrogate model of MSP vs. steam cracker product composition.[229] At each iteration, three new candidate compositions were proposed by optimizing the surrogate model. Three points were chosen to balance exploration and interpolation. For each new candidate, steam cracker product yields were predicted, incorporated into a retrofit-constrained flowsheet, and evaluated through TEA. Iterations were continued until convergence, defined as a change of less than 0.1% in MSP between successive iterations.

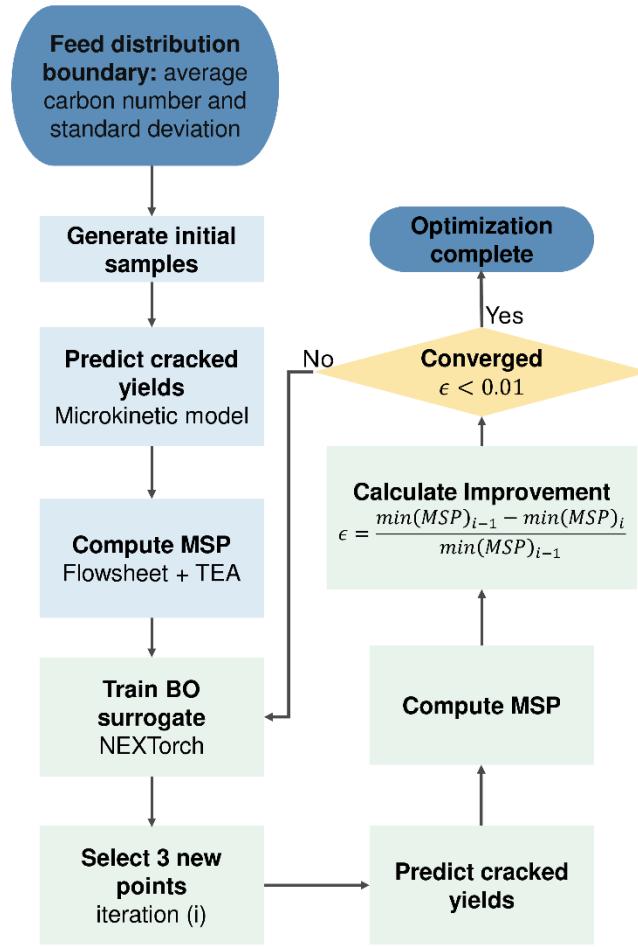


Figure 6.1: Multiscale retrofit-active learning methodology utilized to obtain optimal PW naphtha composition. BO = Bayesian optimization.

6.4 Results and discussion

6.4.1 Conventional naphtha cracking process

The base-case naphtha steam cracking process (Figure 6.2) was adapted from *Spallina et al.[62]* The overall process consists of four main sections: (1) steam cracking, (2) primary fractionation, (3) compression and cryogenic cooling, and (4) product separation. In the first section, naphtha and steam are fed to the cracking

furnace train at a steam-to-naphtha ratio of 0.5 kg/kg. Steam cracking is carried out at near-atmospheric pressure and 850 °C, producing light olefins, benzene, toluene, and xylenes (BTX), as well as fuel gas. The hot product gas is rapidly quenched to approximately 200 °C in a transfer line exchanger (TLE). The effluent is further cooled and sent to a primary fractionator, where heavy hydrocarbons ($\geq C_9$) are removed. The lighter fraction ($< C_9$) is subsequently cooled and flashed, followed by water removal using a molecular sieve adsorption column. The dry gaseous stream is compressed to 31 bar in a multistage intercooled compressor train. Condensed liquid streams from the compression are directed to the BTX recovery section. In the final separation section, the compressed gas is cooled and fed to a de-methanizer, where fuel gas is removed as the overhead product. The bottom stream is then sent to a de-ethanizer. The de-ethanizer bottom is sent to a de-propanizer, and the de-propanizer bottom is subsequently fed to a debutanizer. Heavy liquid products from these downstream columns are routed for BTX recovery. The overhead stream from the de-ethanizer is first sent to a selective hydrogenation reactor, where acetylene is hydrogenated to ethylene, and is then fed to a C_2 splitter for ethylene recovery. Similarly, the overhead stream from the de-propanizer is sent to a hydrogenation reactor to convert methylacetylene and propadiene to propane, followed by a C_3 splitter to recover polymer-grade propylene. The de-butanizer bottom consists of C_5 - C_8 and is primarily rich in aromatics, therefore called BTX-rich Pygas. Figure 6.3a shows a typical conventional naphtha composition, with the gas product composition shown in Figure 6.3c. The number of stages and reflux ratio of each column are summarized in Table E.2.

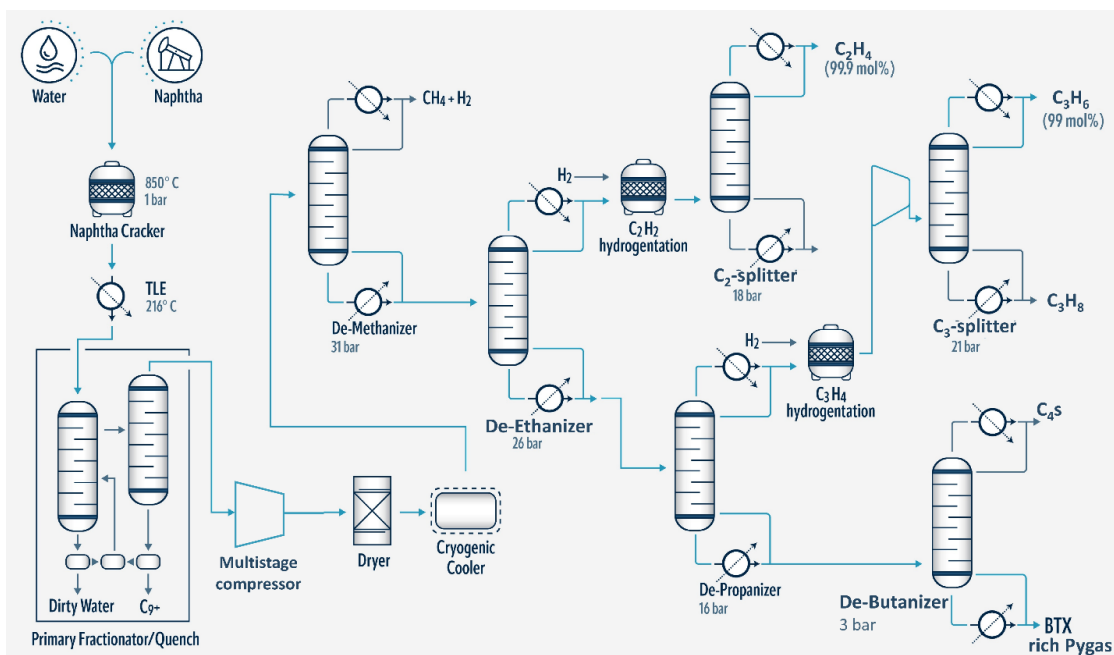


Figure 6.2: Schematic layout of the conventional naphtha steam cracking plant. Pygas = pyrolysis gasoline. TLE = Transfer line heat-exchanger, CH_4 = methane, H_2 = hydrogen, C_2H_2 = acetylene, C_2H_4 = ethylene, C_3H_4 = methyacetylene, C_3H_6 = propylene, C_3H_8 = propane.

6.4.2 Integration of Plastics-waste (PW) Naphtha into Existing Assets

As described in Section 6.3.1, a retrofit integration strategy was adopted for various scenarios (summarized in Table 6.1). Figure 6.3a indicates that conventional naphtha is composed of paraffins (~73 wt%), with notable fractions of olefins and naphthenes (~21 wt%) and a smaller fraction of aromatics (~6 wt%). By contrast, PW naphtha (Figure 6.3b) is more than 98 wt% paraffinic (composition taken from *Sun et al.*[49]). This compositional variation has important ramifications for product distribution and economics.

Table 6.1: Summary of benchmark and retrofit scenarios.

Case	Mode	PW naphtha feed of total fraction (wt%)	Conventional naphtha furnace temperature (°C)/residence time (ms)	PW naphtha furnace temperature (°C)/residence time (ms)
Benchmark	Conventional	0	850/ 80	
Scenario 1	Co-feed	5	850/ 80	
Scenario 2	Co-feed	25	850/ 80	
Scenario 3	Dedicated furnace	5	850/ 80	850/ 80
Scenario 4	Dedicated furnace	25	850/ 80	850/ 80
Scenario 5	Dedicated furnace	25	850/ 80	900/ 25

We consider two broad cases: PW naphtha co-fed with conventional naphtha or processed in a separate furnace at fractions of 5 or 25 wt% of the total. While a new cracker is not practically required because multiple reactors run simultaneously, adding a new furnace provides a higher capital expense than necessary (worst case). (Scenarios summarized in Table 6.1). In Section 6.4.2-6.4.3, we assume this worst-case scenario, and fix the steam-to-naphtha mass ratio to 0.5 and the total (dry) naphtha feed rate to 488 t/h. Microkinetic simulations, discussed below, show that the maximum light-olefin yield (C_2 and C_3) for PW naphtha is achieved at 900 °C and ~25 ms (refer to Figure E.1). Based on this, we set the cracking temperature and residence time to 850 °C and 80 ms, respectively, in all cases except Scenario 5 (900 °C, 25 ms). To achieve a residence time of 25 ms, the tube lengths in the furnace can be adjusted. We can also achieve a 25 ms residence time in old furnaces by reducing the number of tubes used while keeping the total feed rate constant.

The steam cracker product distributions that enter the primary fractionator, predicted by the microkinetic model at the temperature and residence time shown in Table 6.1, are presented in Figure 6.3c. Incorporating PW naphtha increases the light-olefin yield, most notably ethylene, from 32.6 wt% (benchmark) to 35.8 wt% (Scenario 5). Propylene yield changes only slightly (15.3–16.3 wt% across cases). Methane increases modestly when PW naphtha is used, and the cracking severity (temperature) increases. By contrast, benzene decreases from 8.5 wt% (benchmark) to 7.2 wt% (Scenario 5), indicating a reduction in aromatics. Because the operating conditions were selected to maximize light-olefin yield, the propylene-to-ethylene ratio (cracked severity)[163] changes only modestly across scenarios.

Overall, the results underscore clear trends. Notably, increasing the fraction of PW naphtha increases ethylene yield, regardless of the feeding strategy. A separate furnace is preferable to cofeeding due to nonlinear interactions among components in the steam cracker; this is the most impactful strategy for increasing ethylene yield. Finally, high temperatures drive cracking severity, and short residence times suppress benzene production, consistent with prior studies.[20, 146, 160, 161, 230]

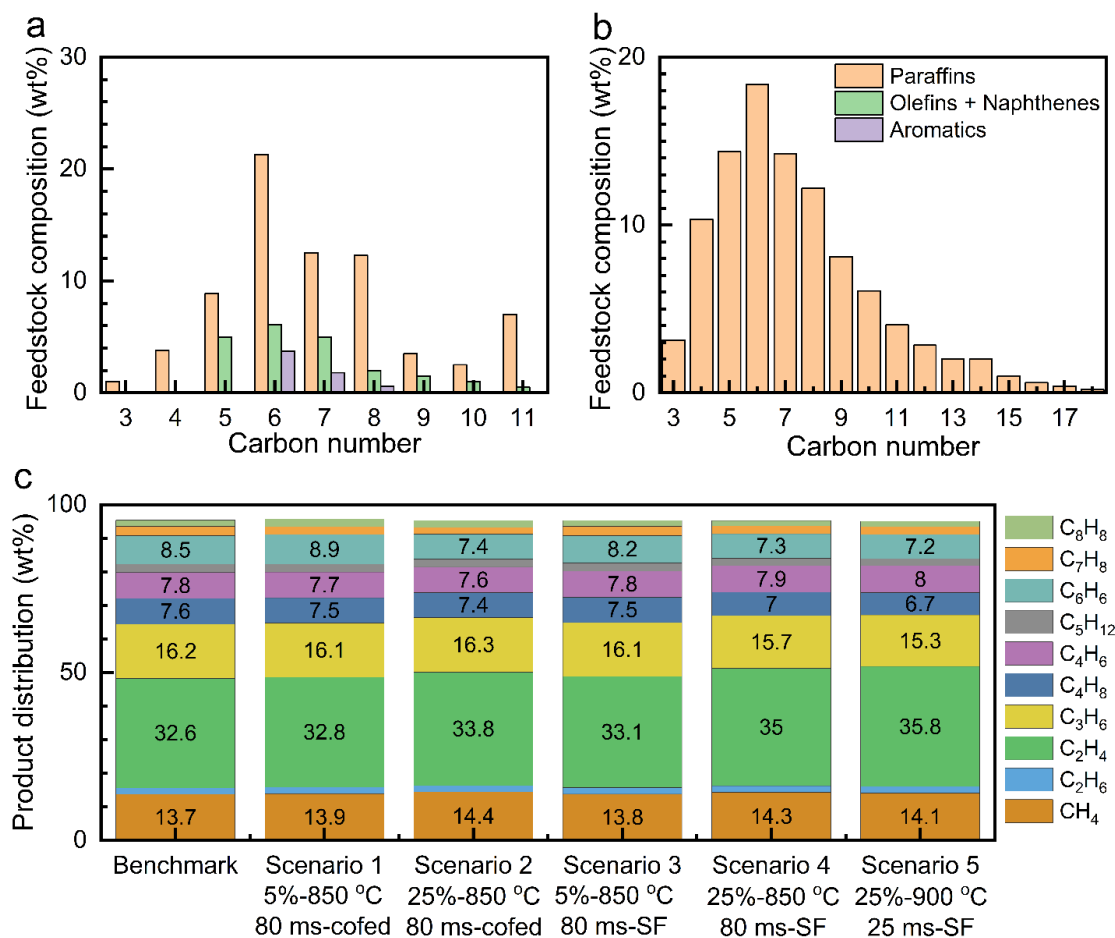


Figure 6.3: Typical naphtha and corresponding steam cracker product distribution. Carbon-number distribution of (a) conventional naphtha and (b) plastics-waste naphtha, adapted from Sun et al. (LDPE hydrocracking over 5 wt% Ni/BEA at 300 °C, 30 bar H₂, and 1 h). (c) Microkinetic model predicted product distribution before the primary fractionator (dry basis) for scenarios summarized in Table 6.1 and also abbreviated here (only compounds at > 2 wt% are shown). SF=separate furnace.

6.4.3 Economic performance

TEA was performed across scenarios using the highest cost of PW naphtha (\$810/t) reported by Vance et al[52] (Figure 6.4). The results show that retrofitting the conventional naphtha cracker with PW naphtha moderately increases the capital cost

due to the higher-heat-duty furnace train, which increases the furnace train cost, while the total manufacturing cost remains relatively unchanged. Specifically, the TCI increases from \$730 M in the benchmark case to \$901–930 M for the dedicated-furnace scenarios (Figure 3a). The co-feed Scenarios 1–2 require limited modifications and therefore increase the TCI to a lesser extent. This capital penalty can be mitigated using an existing cracker rather than installing a new unit.

Despite higher capital costs, TCM remains within a relatively narrow range of \$2294–2564 M/yr, indicating that the integration of PW naphtha does not substantially alter a plant's overall operating burden. The MSP follows a similar trend across most scenarios but decreases in Scenario 5 to \$ 1389/t, compared with \$1396/t (benchmark case), despite a higher TCI. This improvement is primarily attributed to the higher light-olefin yield from PW naphtha cracking at 900 °C, thereby enhancing the value of the product slate. By contrast, Scenarios 1, 2, and 4 exhibit higher MSP values because the increased cost of PW naphtha is not fully offset by gains in olefin production.

The operating-cost breakdown in Figure 6.4b indicates that feedstock is the dominant contributor to operating costs across all scenarios and that this share increases when using a larger fraction of PW naphtha, due to its higher cost relative to conventional naphtha (as evident in Scenarios 2, 4, and 5). By-product credits remain of similar magnitude across cases. Heating costs, however, decrease noticeably upon incorporating PW naphtha, primarily due to changes in product composition that affect downstream separation duties. In particular, the more olefin-rich and less aromatic product slate reduces the burden on separation. Consistent with the product distributions shown in Figure 2, lower-temperature operation favors the formation of

fuel gas and BTX, whereas higher-severity/lower-residence-time cracking shifts the product slate toward light olefins. Scenario 5 achieves the most favorable balance between product value and operating cost. Because feedstock costs dominate OPEX, the economics of the retrofit scenarios are governed primarily by the cost of PW naphtha. As reported by *Vance et al.*, [52] this cost is highly sensitive to the collection and sorting expense of plastics, which are strongly influenced by population density of the plastic-to-naphtha conversion location. [25, 216] Therefore, a sensitivity analysis on collection and sorting costs is required to determine the break-even cost and the economically viable range for the integration of plastic-derived naphtha. This analysis can further guide the selection of plastic-to-naphtha conversion location and clarify the conditions under which this process can become economically competitive.

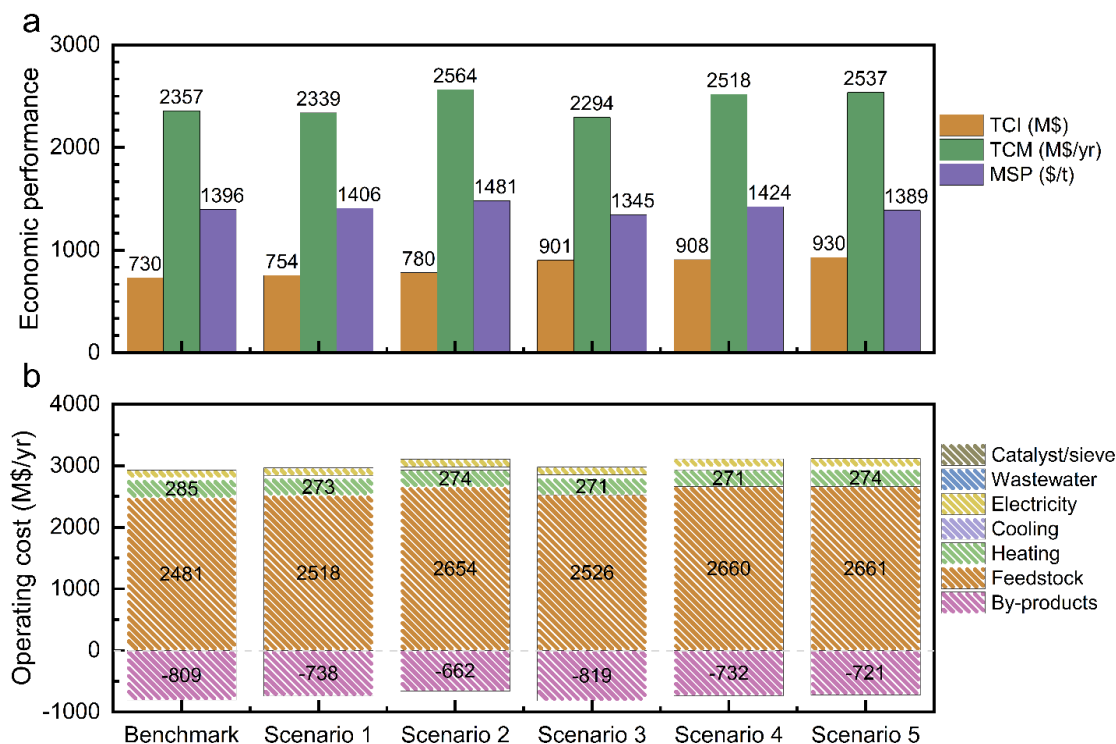


Figure 6.4: Economic performance of various scenarios evaluated using a PW naphtha price of \$810 /t. (a) Total capital investment (TCI), total cost of manufacturing (TCM), and minimum selling price (MSP) for conventional naphtha cracking and the five retrofit scenarios. (b) Operating-cost breakdown showing contributions from feedstock, heating, cooling, electricity, wastewater, catalyst/sieve, and by-product credits. A negative value for by-products means we earn credits by selling them.

6.4.4 Cost of plastic-derived naphtha

Because feedstock cost dominates the operating expense of the retrofit cases, the MSP of olefins is strongly governed by the cost of PW naphtha. This cost depends in part on plastics collection and sorting, for which we used population density as a first-order proxy..[52] This choice follows *Hernandez et al.*,[216] who reported that the cost of PW collection and sorting is a function of the population density of the collection and sorting region. The work also showed that denser regions tend to

benefit from lower per-unit collection and sorting costs due to shorter transport distances, larger throughput, and more efficient logistics. In adopting this relationship, we assume that population density correlates with the scale and effectiveness of local collection infrastructure, while recognizing that it does not explicitly account for regional differences in sorting quality, contamination level, policy support, or transportation mode. The resulting collection-and-sorting cost was then incorporated into the linear fit reported by *Vance et al.*[52] to estimate the MSP of PW naphtha. Scenario-specific linear correlations were subsequently developed (Table E.3) to relate PW naphtha cost to olefin MSP, thereby allowing prediction of olefin MSP as a function of population density. Accordingly, this analysis is intended as a screening tool for comparing regions and scenarios, rather than as a site-specific economic forecast.

Figure 6.5 recasts the economics of retrofit integration vs. population density. As the population density increases, the MSP decreases due to lower collection and sorting costs. The effect is most pronounced for higher PW naphtha utilization. Three economic regimes emerge from Figure 4. In low-population-density areas, the benchmark remains the lowest-cost option because the collection and sorting penalty makes PW naphtha expensive. In areas with intermediate population density, Scenario 3 is the most favorable, indicating that a dedicated furnace can be competitive. In higher population density, Scenario 5 yields the lowest MSP, indicating that once PW naphtha can be sourced at a sufficiently low cost, the dedicated 900 °C steam cracker's higher light-olefin yield outweighs its added capital. In this sense, population density acts as a proxy for feedstock accessibility, while the crossover points define the economic thresholds for viable retrofit operation.

This framework also identifies likely U.S. states where we should establish PW recycling sites to support economic integration. Using 2020 U.S. Census state densities,[231] very low-density states, such as Wyoming are near 2.3 inhab/km², while Oregon is about 17 inhab/km², Texas about 43 inhab/km², California about 98 inhab/km², Ohio about 112 inhab/km², New York about 166 inhab/km², and New Jersey about 488 inhab/km². The U.S. average is about 362.3 inhab/km². These values suggest that sparsely populated western states are more likely to fall into region 1, where conventional naphtha is preferred, and mechanical recycling should be chosen, if possible. Moderately populated states, such as Texas, lie closer to the transition into retrofit viability. In these states, modest PW chemical recycling sites should be established to generate PW naphtha that can substitute for at least 5 wt% of conventional naphtha. More densely populated states, such as California, Ohio, New York, and especially New Jersey, fall well within the range where retrofit scenarios become increasingly attractive, with the highest-density states favoring Scenario 5. Sites capable of producing >25 wt% conventional naphtha should be developed. Figure 6.5 can also be used to determine the maximum PW naphtha MSP that refineries can tolerate while still economically benefiting from integration, in addition to potential carbon-credit advantages. Based on the crossover points that demarcate regions 2 and 3, the maximum viable PW naphtha costs are approximately \$1100/t and \$850/t (Figure 6.5 and Figure E.2), respectively. This result shows that PW naphtha integration can be beneficial even at a price premium.

The above discussion considers state-based analysis. Given the variation in population density across states, we suggest focusing on densely populated cities where most plastic is used and discarded. There, the density can exceed 10,000

people/km². Assuming a recycling facility handling ~100,000 t of plastics/yr (100 kta), this would imply we need about 3 such plants near Houston and 10 near New York City, for context. For all big cities, the MSP from converting plastics into naphtha, which is then retrofitted into existing assets, will be lower than the reference case.

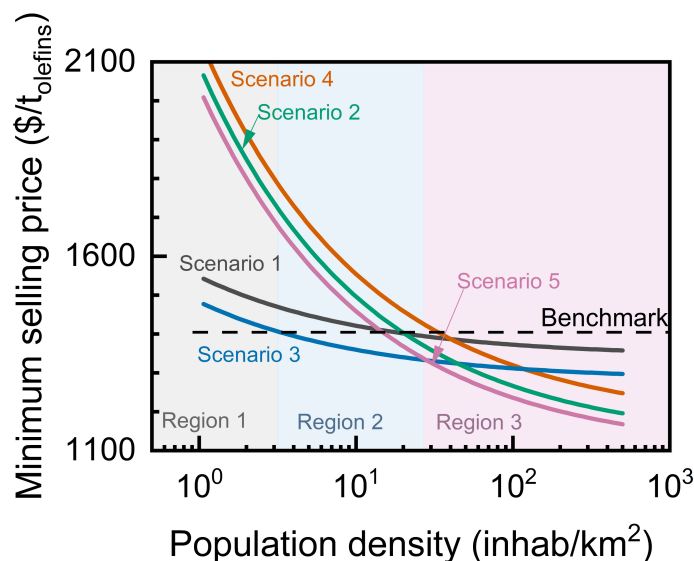


Figure 6.5: MSP of olefins as a function of population density for the benchmark and retrofit scenarios. The benchmark is shown as a horizontal dashed line, while Scenarios 1–5 represent retrofit cases with different strategies for integrating PW naphtha. The shaded regions indicate the scenario with the lowest MSP at a given population density: Region 1, benchmark; Region 2, Scenario 3; and Region 3, Scenario 5.

6.4.5 Active Learning-guided PW Naphtha Composition

While previous analysis considered a single PW naphtha composition, plastic hydrocracking can produce a spectrum of naphtha compositions. To generalize the findings of this study, an active-learning framework was used to identify PW naphtha

compositions that maximize the economic benefit of integration into conventional naphtha cracking.

The feed was parameterized by the average carbon number and the standard deviation of the carbon-number distribution, enabling efficient exploration of a broad range of literature-reported PW naphtha compositions within a reduced design space. For each sampled composition, microkinetic model steam cracker product yields were input into the retrofit-constrained flowsheet and evaluated, thereby directly linking feed composition and process economics. Less than 20 calculations were used for this task. Figure 6.6 summarizes the active-learning-guided composition space for PW naphtha and the resulting tradeoffs among olefins, BTX, fuel gas, and coking tendency. While PW naphtha composition directly influences product yields, production rates are reported here because they are more relevant to process economics, which is the focus of this analysis. In particular, production rates capture both upstream selectivity effects and downstream process impacts, including separation losses and gains from selective hydrogenation.

The olefin response surface (Figure 6.6a) shows that narrow and low carbon-number distributions maximize light olefin formation. Olefin production decreases as the feed becomes heavier, but partially recovers at high standard deviations, where the broader distribution reintroduces lighter fractions. BTX follows the opposite trend (Figure 6.6b): it is lowest for light, narrow feeds and increases with both average carbon number and distribution width, reaching its highest values in the heavier and broader region of the design space. Fuel-gas formation (Figure 6.6c) increases toward intermediate-to-heavy and broad distributions, consistent with stronger secondary cracking of a diverse hydrocarbon mixture. Together, these maps show that light feeds

favor primary olefin production, whereas heavier and broader feeds promote by-product formation through aromatization and secondary cracking pathways.

Coking tendency introduces an additional design constraint. Because naphthalene has been widely used as a surrogate for coke precursors,[147, 230, 232] it was used here as a proxy for coking tendency in the dedicated plastic-derived naphtha furnace. The model predicts that conventional naphtha produces about 0.4 wt% naphthalene, whereas PW naphtha yields substantially lower values (Figure 6.6d), indicating that PW naphtha can reduce coke formation by more than 50%. As with BTX and fuel gas, naphthalene generally increases with heavier feeds of broader distribution, reflecting the greater tendency of such compositions to form polyaromatics. By contrast, light naphthas with a narrow distribution favor olefins and minimize naphthalene formation in addition to a higher light-olefin selectivity. A reduced coking tendency further implies longer furnace train run lengths, less steam, and decreased decoking frequency, representing improved operability and a higher on-stream factor, economic benefits not accounted for in the current study.

Because the economics of retrofit integration depend on both olefin production and by-product value, at least based on the current market needs, the most favorable composition is not the one that maximizes olefins alone (Figure 6.6e). Instead, a PW naphtha centered near an average carbon number of 11 and a standard deviation of 4 provides the best overall compromise, maintaining relatively high olefin production while increasing valuable BTX and fuel-gas co-products, and substantially lowering naphthalene formation compared with conventional naphtha. This result suggests that hydrocracking should be tuned to target a composition window that balances olefin

yield, by-product value, and coking tendency for downstream steam-cracker integration.

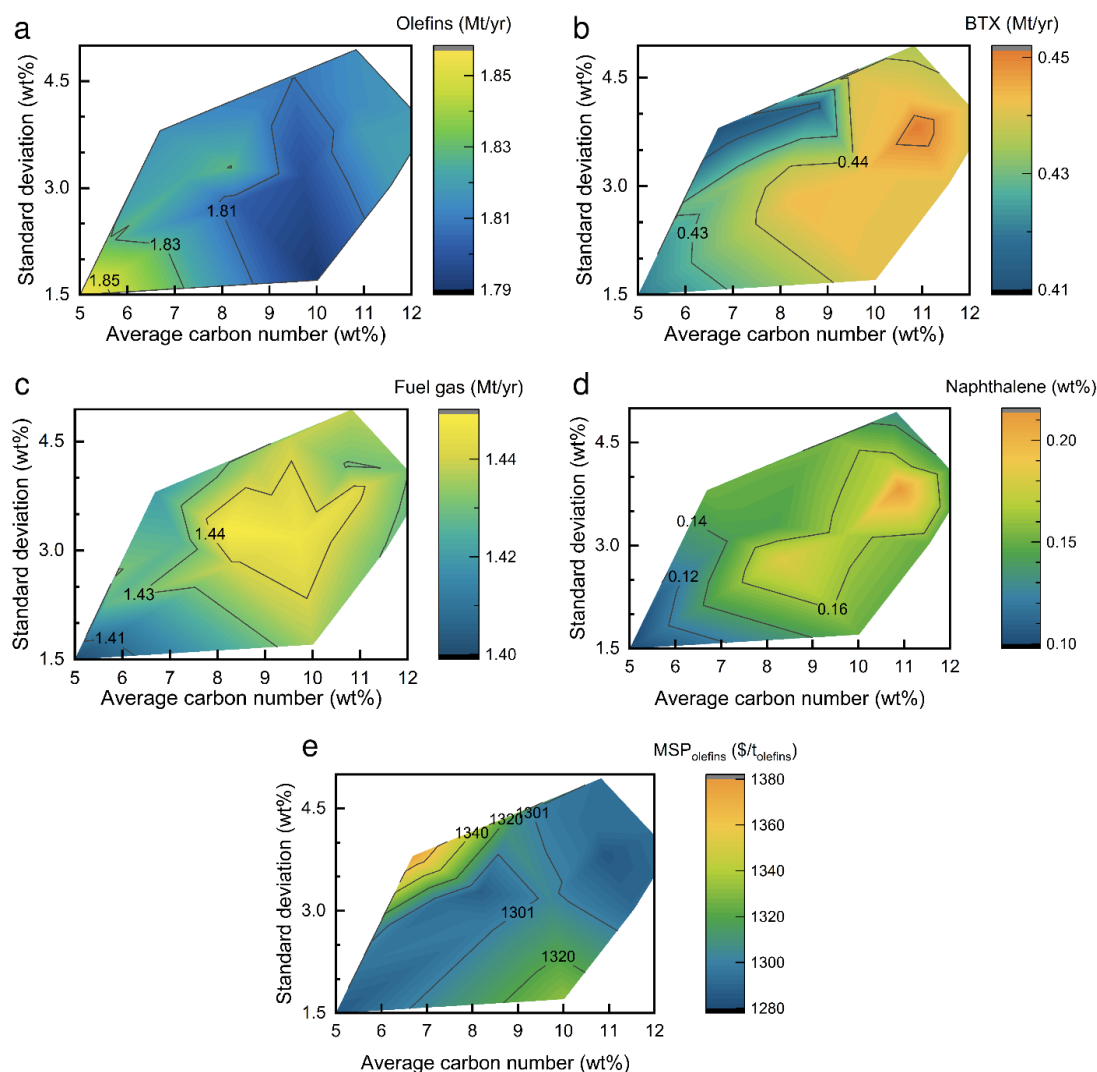


Figure 6.6: Composition-dependent product map for PW naphtha. Predicted production rates of (a) olefins, (b) BTX, (c) fuel gas, and (d) naphthalene product yield and (e) minimum selling price (MSP) of olefins as a function of the average carbon number and standard deviation of the PW naphtha distribution. Contours were generated from the evaluated design space using the coupled workflow.

Figure 6.7a shows the optimal PW naphtha composition obtained from active learning. This composition was fed into Scenario 5, assuming the naphtha cracking has one or more existing cracking furnaces for PW naphtha and that feedstock is sourced from high-density regions, such as New Jersey. Under these conditions, Figure 6.7b shows the steam cracker product distribution before the primary fractionator (dry basis). The product stream contains 35.8 wt% ethylene and 15.5 wt% propylene, with the remainder comprising methane, BTX, and fuel gas. This balanced product slate translates to a TCI of \$725, a TCM of \$2358 M/yr, and an MSP of \$1296/tonne (Figure 6.7c). It is important to note that this result is sensitive to the selling price of BTX and fuel gas; for example, a 20% reduction in the selling price of BTX would shift the optimal naphtha composition to a lower average carbon number and a broader distribution to increase fuel gas and olefin production. Figure 6.7d shows that sourcing PW naphtha from high-population-density states significantly reduces feedstock costs, and optimal naphtha composition reduces the energy burden on separations. These results show that PW naphtha can provide a tangible economic advantage when integrated into existing steam-cracking infrastructure under favorable collection, sorting, and retrofit conditions.

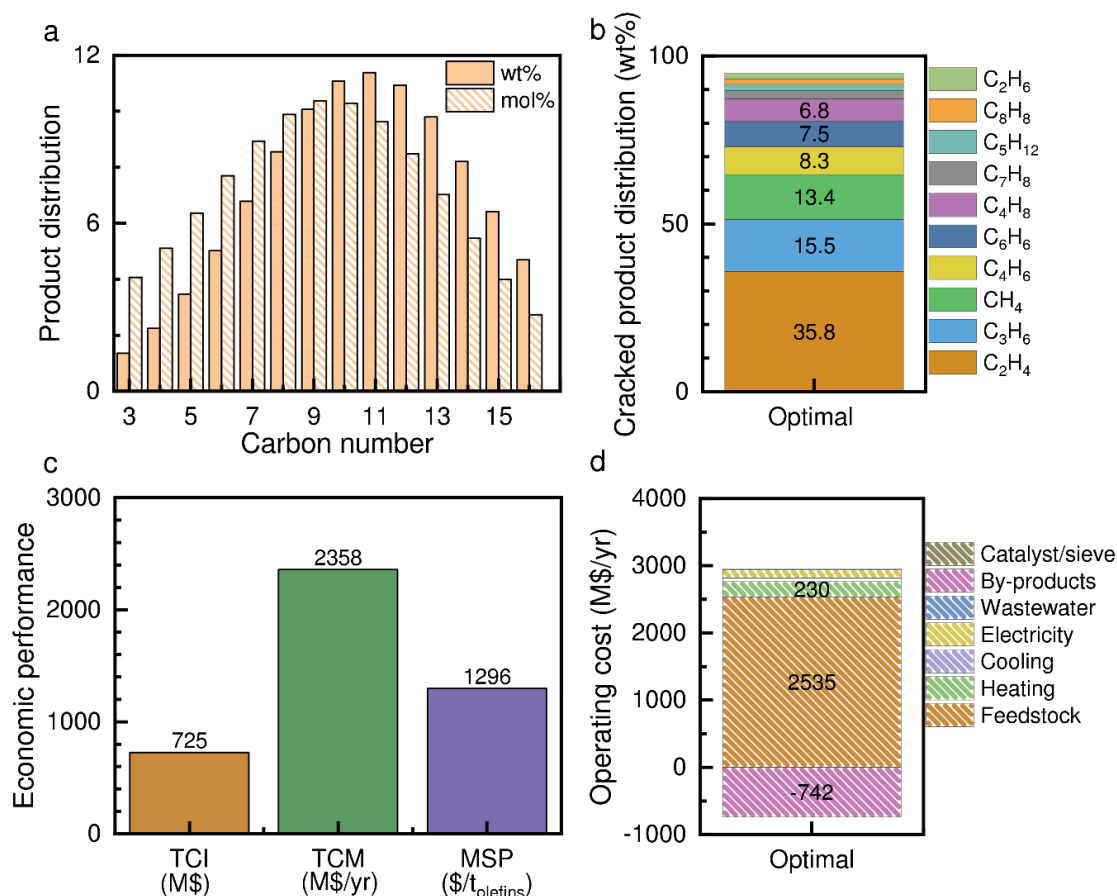


Figure 6.7: PW naphtha composition obtained from active learning and its performance under best-case retrofit conditions. (a) PW naphtha composition obtained from active learning in wt% and mol%. (b) Cracked gas distribution before the primary fractionator under the best-case retrofit scenario (dry basis). (c) Economic performance and (d) operating cost of the optimized case

6.5 Discussion

Additional reductions in MSP and TCM are possible by increasing hydrocracking naphtha yield, extending catalyst applicability to a broader range of PW streams, reducing catalyst cost, and improving catalyst lifetime. Downstream, PW naphtha may require less steam than conventional naphtha due to reduced coking. To

probe this effect, the total olefin and naphthalene yields were calculated as the dilution steam ratio was decreased during cracking (see Figure E.3). Figure E.3 suggests that reducing the dilution ratio to 0.3 – 0.4 kgsteam/kg naphtha can decrease naphthalene production, but it also decreases olefin production. We hypothesize that this is due to the high severity requirement that increases with dilution. Higher severity at high dilution increases naphthalene yields; it decreases at a moderate ratio, then increases at lower dilution, as the partial pressure of olefins is high enough to promote naphthalene formation. Therefore, detailed studies are required to find the new optimal dilution for PW naphtha. Together, these results suggest that further optimization of hydrocracking performance, steam demand, water management, coking behavior, and heat integration could reduce both MSP and TCM beyond the values reported here.

We also assessed the economics of a ground-up plant designed specifically for the optimized PW naphtha, based on 122 t/h of PW naphtha, 366 t/h of conventional naphtha, and a steam dilution ratio of 0.5 kg steam/kg naphtha. In contrast to the retrofit cases, such a plant must include additional capital, e.g., land acquisition and startup, each commonly estimated as 4% of total depreciable capital. These costs have little influence on MSP at the zero-net-present-value condition, but they do increase TCI, which is often a decisive metric in industrial investment decisions. The ground-up plant requires a TCI of \$897 M, which is \$172 M higher than the optimized retrofit case. Although the tailored design could lower MSP by \$2–5/ton of olefins, mainly through reduced primary-fractionator energy demand, this translates to only about \$4–10 M/yr of additional profit for a 2 Mton of olefins per year facility. As a result, recovering the higher capital outlay would require ~20 years, strongly disincentivizing construction and underscoring the value of retrofit-based integration.

6.6 Conclusion

This work shows that PW naphtha can be integrated into existing industrial steam crackers (retrofitting). By coupling detailed microkinetics, process simulation, techno-economic analysis, and active learning, we established how the feed composition, integration strategy, and collection and sorting conditions jointly determine economic performance. Across retrofit cases, separate processing of PW naphtha in a dedicated furnace at higher severity provided the greatest improvement in product value, while population density emerged as a practical proxy for collection and sorting costs and, therefore, for the economic viability of feedstock sourcing.

The analysis yields three industry-relevant conclusions. First, the capital penalty of integration is modest in a retrofit setting and may be further reduced in real plants that already operate multiple furnaces in parallel. Second, PW naphtha can remain economically attractive even at a price premium over conventional naphtha, provided that it is sourced from sufficiently favorable regions and routed through the right process configuration. Third, the optimal PW naphtha is not the composition that maximizes olefins alone, but one that balances olefins with BTX and fuel gas to improve overall process economics. Under the best-case industrial scenario identified here - incorporating specific feedstock costs, byproduct credits, and operating set-points - the optimized feed composition results in an MSP of \$1296 /t_{olefins}. This represents a \$100/ton reduction (approximately 7.2%) relative to the conventional naphtha benchmark, confirming the value of the proposed framework for composition-aware feed design and targeted asset utilization.

At the same time, this study highlights important practical limitations that must be addressed before broad industrial adoption. The present population-density framework assumes that higher population density correlates with better collection and

sorting infrastructure and with larger, more efficient facilities. In practice, this relationship is imperfect, and population density alone cannot fully capture local differences in bale quality, sorting efficiency, contamination level, logistics, or policy support. Collection, sorting, and transportation costs remain major uncertainties. Well-sorted polyethylene-rich bales can already command substantial prices, and costs rise significantly as higher purity is required. At the scales relevant here, hydrocracking costs are also expected to remain substantial, and transportation can add another major penalty, especially when naphtha must be shipped over long distances or by sea. As a result, the full delivered cost of plastics waste-derived naphtha may remain high in real settings, even if the downstream cracking configuration is favorable.

Several directions for future work, therefore, emerge. Upstream, the optimal naphtha composition identified here should be translated into achievable hydrocracking operating conditions of catalyst identity, temperature, residence time, and hydrogen pressure. Future studies should also explicitly account for heteroatoms and contaminants in plastic-derived naphtha, since sulfur-, nitrogen-, oxygen-, chlorine-, and metal-containing species could affect catalyst stability, coking, separations, corrosion, and overall process economics. Potential mitigation strategies include improved feed pretreatment and sorting, guard beds, hydrotreating or hydrodeoxygenation steps, adsorptive cleanup, chlorine removal, and catalyst formulations that are more tolerant to impurities. More broadly, future techno-economic studies should replace simple population-density proxies with geographically resolved supply-chain models that explicitly include collection quality, bale composition, transportation mode, distance, and regional infrastructure maturity.

Taken together, these results position PW naphtha as an industrially relevant intermediate for the production of circular olefins and offer a concrete roadmap for integrating chemical recycling with established steam-cracking assets. They show the best path for retrofit integration, the most valuable naphtha compositions, and the upstream and downstream constraints that need to be addressed.

Chapter 7

CONCLUSIONS AND OUTLOOK

7.1 Overall summary and key conclusions

This dissertation focused on one central idea: decarbonizing olefin manufacturing requires addressing both how heat is supplied and where the carbon feedstock comes from. Decarbonization will require new approaches to reactor design, material selection, feedstock upgrading, and industrial integration. With that motivation, this thesis developed a multiscale chemical reaction engineering framework that connects electrothermal reactor design with circular feedstock utilization for decarbonized olefin manufacturing.

Chapter 2 of the dissertation established the transport and design principles for Joule-heated systems. This work demonstrated that carbon-fiber-paper-based systems can heat rapidly and reach high local temperatures while limiting unnecessary heating of the flowing gas. At the same time, it identified important design limitations, particularly buoyancy-driven recirculation and reverse flow under typical operating conditions. These results made it clear that Joule-heated reactors are not simply fast heating devices; they are transport-sensitive systems whose performance depends strongly on reactor geometry, heating-element dimensions, flow conditions, and electrical operating parameters.

Chapter 3 extended this understanding from the reactor scale to the materials scale. That work showed that the performance of a Joule-heating element is fundamentally governed by its intrinsic material properties and structure. Electrical

conductivity and volumetric heat capacity were found to control heating rate, while thermal conductivity played a major role in determining temperature uniformity. Carbon-based materials, especially carbon fiber paper and graphite, emerged as promising candidates. At the same time, this study revealed important structural tradeoffs. Porosity and engineered architectures can improve transport, but they can also create current-density non-uniformities and localized hotspots that threaten material stability.

These electrothermal design principles were then applied to a specific and important case study: ethane cracking for ethylene production. Chapter 4 showed that internal Joule heating can access operating windows that are difficult to achieve in conventional furnace-based systems, particularly at high temperatures and very short residence times. Under such conditions, ethylene yield improves while methane and aromatic byproducts are suppressed. The process-level analysis further suggested that internally heated cracking can reduce capital investment and lower emissions when paired with low-carbon electricity.

The dissertation then turned to the second major decarbonization challenge: circular carbon utilization through plastic waste valorization. A key conclusion from Chapter 5 is that plastic upgrading is not only a catalysis problem, but also a reactor and transport problem. Mixed polymer processing can give poor mixing, and thermal non-uniformity can dominate reactor behavior and obscure catalytic trends. The results showed that conventional magnetic stirring is inadequate for many viscous polymer systems, whereas close-clearance anchor impellers provide much better mixing, thermal uniformity, and circulation. In addition, coaxial impeller configurations were found to improve interfacial renewal in immiscible polymer systems. This chapter

established the hydrodynamic and thermal basis needed to make catalytic plastic valorization more reliable and more scalable.

Finally, this thesis addressed the industrial integration of plastic-derived naphtha into steam cracking. Chapter 6 developed an integrated framework that showed that plastic-derived naphtha can be a valuable feedstock for existing naphtha crackers, but its viability depends strongly on feed composition, sourcing cost, and retrofit strategy. Dedicated-furnace operation was more favorable than simple co-feeding, especially when plastic-derived naphtha was cracked at higher severity. The work also showed that plastic-derived naphtha does not need to match or undercut the price of conventional naphtha to be viable; under favorable conditions, it can remain attractive even at a premium. More broadly, this chapter demonstrated that the value of plastic-derived feeds must be judged not only by product yield, but by how well the new feedstock fits into existing infrastructure under realistic industrial constraints.

Taken together, the broader contribution of this thesis is the connection between low-carbon heat and low-carbon feedstock. Rather than studying electrification and feedstock circularity in isolation, this work linked them through common principles of chemical reaction engineering, transport, and process design. In doing so, it established a framework for olefin manufacturing that is lower in emissions, more energy efficient, and more compatible with a circular carbon economy.

7.2 Outlook

This section proposes future research directions built upon the material presented in this thesis.

7.2.1 Future of internally heated ethane steam crackers

The ethane-cracking results showed that internal Joule heating can access favorable short-contact-time, high-temperature regimes. However, this also highlighted the need for better reactor architecture and a kinetic model. Future work should focus on structured or monolithic Joule-heating elements that reduce temperature gradients and improve heat delivery without sacrificing rapid response. Uncertainty quantification should be performed on the detailed microkinetic model to find the essential reactions that should be incorporated in a lumped kinetic model for reactor design at these high temperatures. Machine learning algorithms can be incorporated to intensify the process. At the same time, quenching must be treated as part of the reactor design rather than as an afterthought, since secondary reactions after the heated zone can erode the gains achieved inside the reactor. Future studies should therefore co-design the heating zone, downstream cooling strategy, and overall flow pattern. Coke formation, pressure drop, and long-term heating-element durability will also need to be studied in more detail before these systems can move toward pilot-scale implementation.

7.2.2 Materials and flow analysis under dynamic operation

The material-selection framework developed in this thesis provides useful design rules, but additional work is needed to make these materials practical under realistic reactor environments. Future studies should examine the long-term structural integrity of heating elements under repeated high-temperature thermal cycling, as mechanical expansion may limit durability and stable operation. The design of electrical connectors and current-collection interfaces also deserves greater attention, particularly for porous and structured elements, where maintaining reliable and

uniform electrical contact is essential for industrial scale-up. Furthermore, this thesis showed that steady-state operation can induce buoyancy-driven recirculation. Under dynamic operation, larger radial and axial temperature gradients may intensify such flow recirculations and significantly alter reactor performance. Future work should therefore investigate these effects systematically in both catalytic and noncatalytic systems, so that the individual contributions of transient thermal gradients, recirculation, and reaction can be clearly understood.

7.2.3 Reactive polymer melt processing

The polymer-mixing chapter focused mainly on nonreactive hydrodynamics and heat transfer, which was an important starting point. The next step is to couple mixing directly with reaction. In real plastic valorization systems, viscosity changes as depolymerization proceeds, products form, and the molecular-weight distribution shifts. This means the flow field, thermal field, and chemistry evolve together. Future work should therefore develop reaction-coupled CFD models and corresponding experiments that account for changing rheology, catalyst distribution, and temperature-dependent transport. It will also be important to better understand viscoelastic effects in systems where operation below the critical Deborah number is not easy to achieve. Ultimately, the goal should be to connect impeller design directly to conversion, selectivity, and catalyst effectiveness rather than to mixing metrics alone.

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Appendix A

SUPPLEMENTARY INFORMATION FOR COMPUTATIONAL INSIGHTS INTO STEADY-STATE AND DYNAMIC JOULE-HEATED REACTORS

A.1 Dimensionless numbers

$$\text{Grasshof number} = Gr = \frac{g\beta(T_s - T_\infty)L^3}{\vartheta^2} \quad (\text{A.1})$$

$$\text{Reynolds number} = Re = \frac{\rho UL}{\mu} \quad (\text{A.2})$$

$$\text{Prandtl number} = Pr = \frac{C_p \mu}{k} \quad (\text{A.3})$$

$$\text{Rayleigh number} = Ra = Gr_x Pr = \frac{\rho\beta\Delta T x^3 g}{\mu\alpha} \quad (\text{A.4})$$

g is gravity, β is the expansion coefficient, L is the length of the element, ϑ is the kinetic viscosity, ρ is the density, U is the velocity, μ is the dynamic viscosity, C_p is the heat capacity, and k is the thermal conductivity.

A.2 Experimental validation of CFD model

Table A.1: Experimental validation of CFD model

Experimental condition	Experimental value	CFD value
Steady state temperature at 30 V	1922 K	1790.2 K
Steady state current – 12.4 V	3.8 A	4.075 A
Steady state current – 14 V	4.61 A	4.5 A
Steady state current – 15 V	5.25 A	5.3 A
Peak of pulsing temperature – 50 V	1473 K	1479.7 K
Minimum of pulsing temperature – 50 V	773 K	716.3 K

A.3 Mesh dependency study

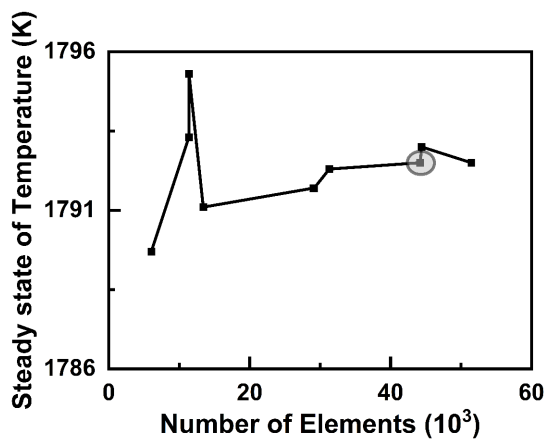


Figure A.1: Mesh dependency study showing the steady state temperature for 30 V, with He flowing at 90 mL/min vs. the number of elements in the mesh. Highlighted mesh configuration used in this study.

A.4 Heating rate

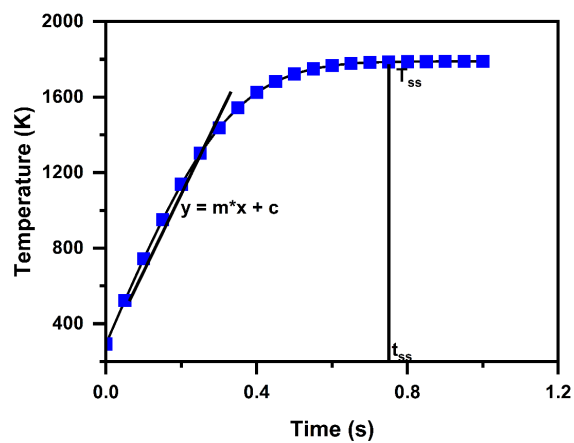


Figure A.2: Temperature of the element vs. time. ($T_{e,ss}$ = temperature at steady state, t_{ss} = time to steady state, and $m = R_h$ = temperature ramp rate). Voltage of 30 V with a He inlet flow of 90 mL/min.

A.5 Results and discussion

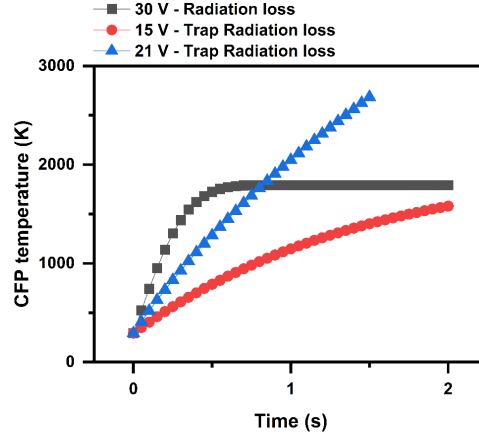


Figure A.3: Impact of trapping radiation using a completely reflective surface over quartz tube on the temperature.

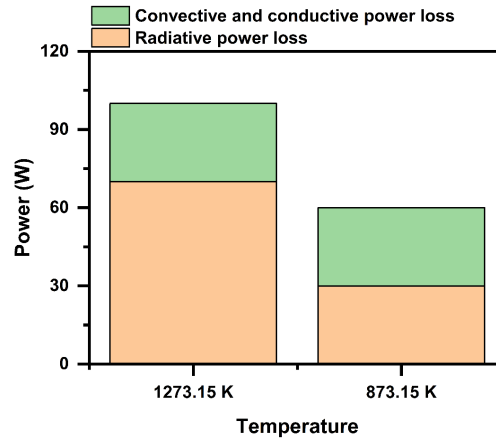


Figure A.4: Power loss contributions when $\overline{(T_{e,ss})} = 1000\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$, using N_2 at 90 mL/min .

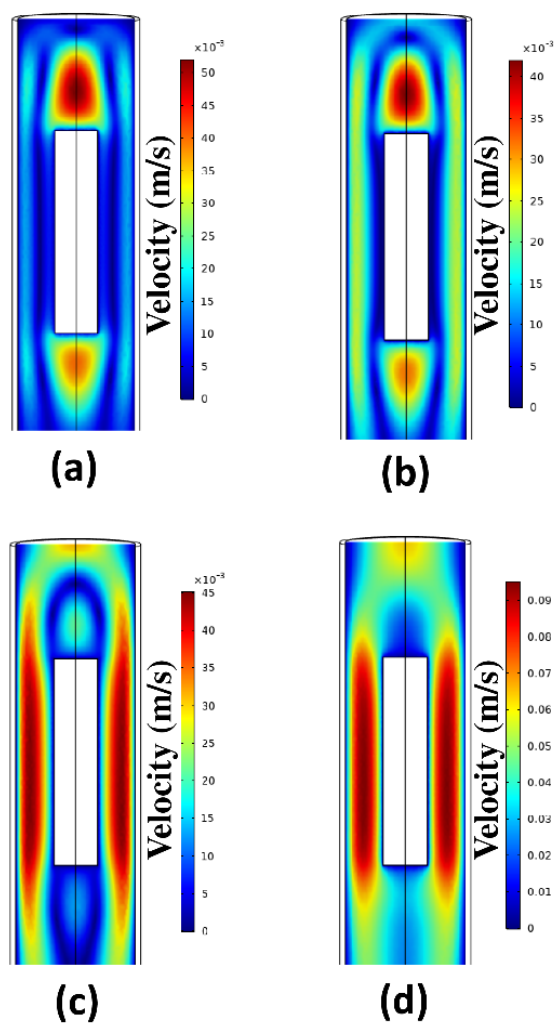


Figure A.5: Flow maps of the magnitude of velocity parallel to the element at steady state for 30 V applied with He flowing at (a) 90 mL/min, (b) 180 mL/min, (c) 360 mL/min, and (d) 720 mL/min.

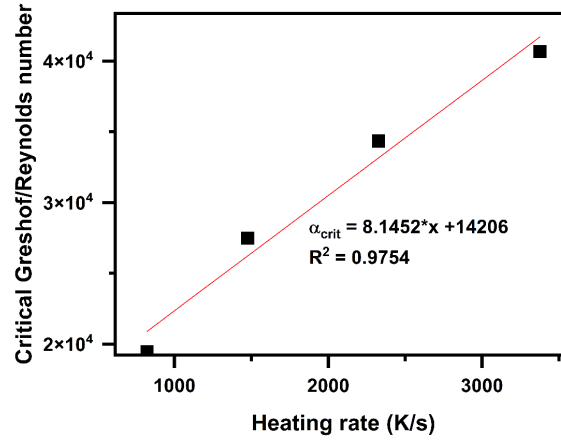


Figure A.6: Variation of the critical value for reverse flow with heating rate.

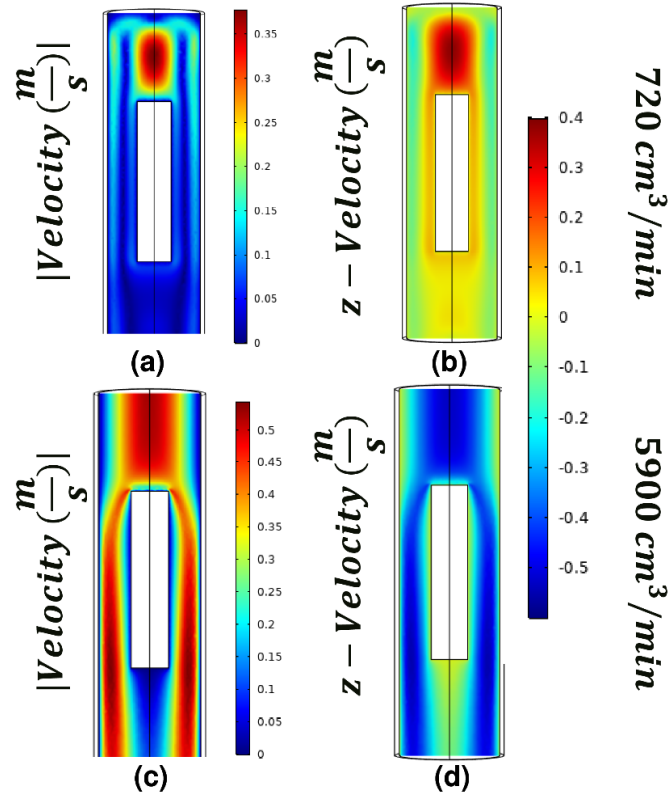


Figure A.7: Flow maps of the magnitude and axial velocity for N₂ for 30 V applied to CFP. (a) Magnitude at 720 mL/min. (b) Axial velocity at 720 mL/min. (c) Magnitude at 5900 mL/min. (d) Axial component at 5900 mL/min.

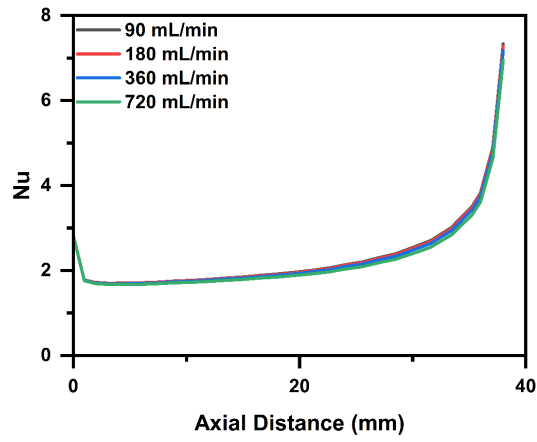


Figure A.8: Impact of inlet flow rate at steady state for 30 V applied to CFP on the Nu number vs. distance from the leading edge of the heating element (assuming incompressibility).

A.6 Heating timescale and steady-state temperature

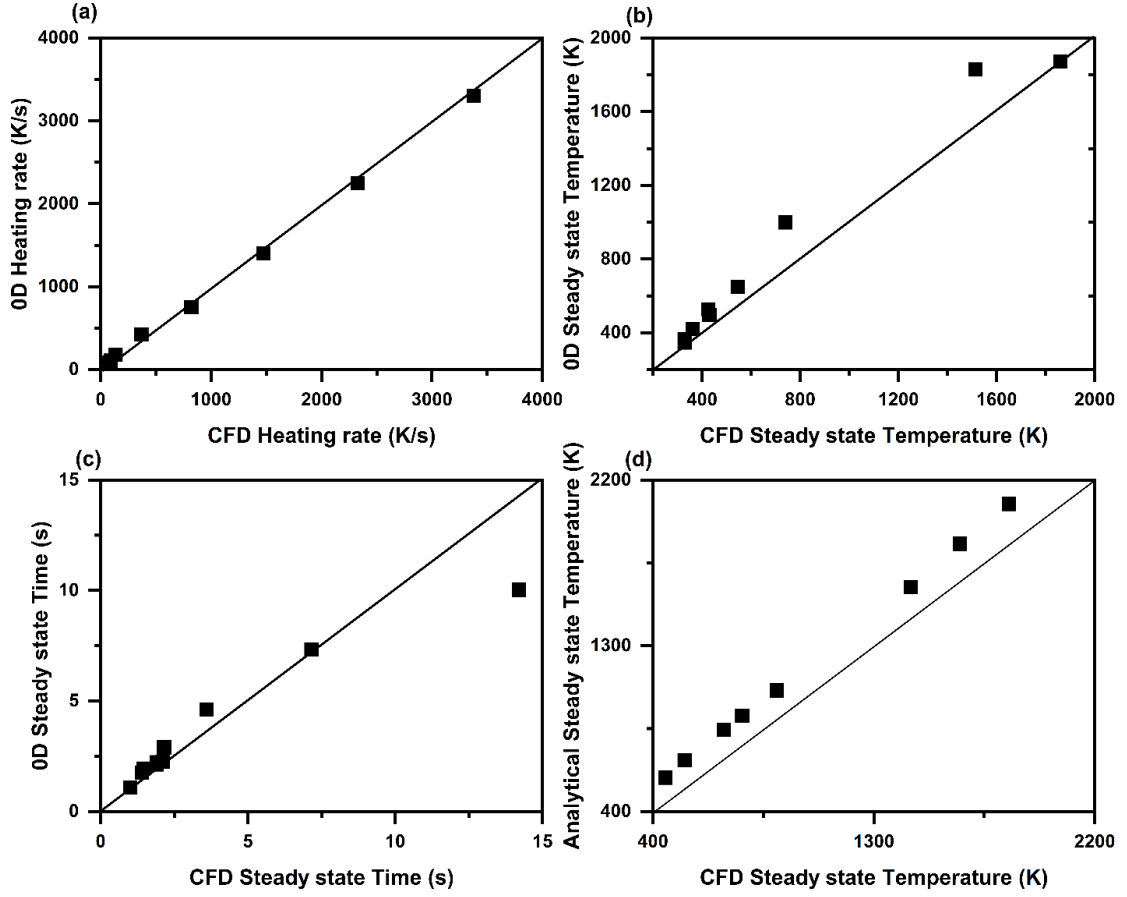


Figure A.9: Parity plots of 0D predicted vs. CFD. (a) Heating rate, (b) temperature at steady state, (c) time to steady state, and (d) temperature. (Voltage applied to CFP = 2-30 V, $L = 38$ mm, $L_{th} = 0.21$ mm, $L_w = 8$ mm, He flowing at 90 ml/min).

A.7 Heating time scale for the gas

Our results show only a minute fraction of the electric heating gets transferred to the gas. To capture the influence of physical properties on the gas outlet temperature (Figure 2.4), we propose Eq. A.5, to calculate t_{eh}

$$t_{eh} = \frac{\rho_g C_{p,g} V_s (T_{e,ss} - T_a)}{hA(T_{e,ss} - T_a)} \sim \frac{\rho_g C_{p,g} LL_{th}}{\kappa Nu_L} \sim \frac{LL_{th}}{a Nu_L} \quad (\text{A.5})$$

Here a is the thermal diffusivity of the system. h can be predicted using Eq. 2.16, and this allows Eq. A.5 to capture all important gas properties. Eq. A.5 assumes that the time constant for a gas film of the same volume as the element to reach $T_{e,ss}$ (gas film is in thermal equilibrium with the element). For instance, *He* flowing with an inlet flow rate of 720 mL/min over the carbon element has $t_{eh} \sim 0.03$ s, which is much smaller than t_0 (~ 1 s) allowing sufficient time to heat up the gas near the element. *Balakotaiah and Ratnakar*⁴⁰ also propose a gas heating time scale from the power generated by Joule heating. Figure 3 indicates that under certain conditions, such as ours, only a fraction of the generated power is absorbed by the gas; most heat is lost directly by radiation.

A.8 Results and discussion – Pulsed Joule heated reactors

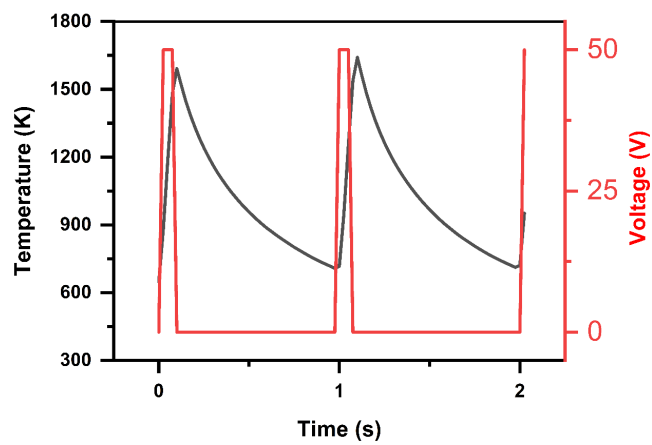


Figure A.10: Temperature profile outcome for the voltage profile applied to the CFP element (50 V applied for 50 ms and 950 ms of cooling time).

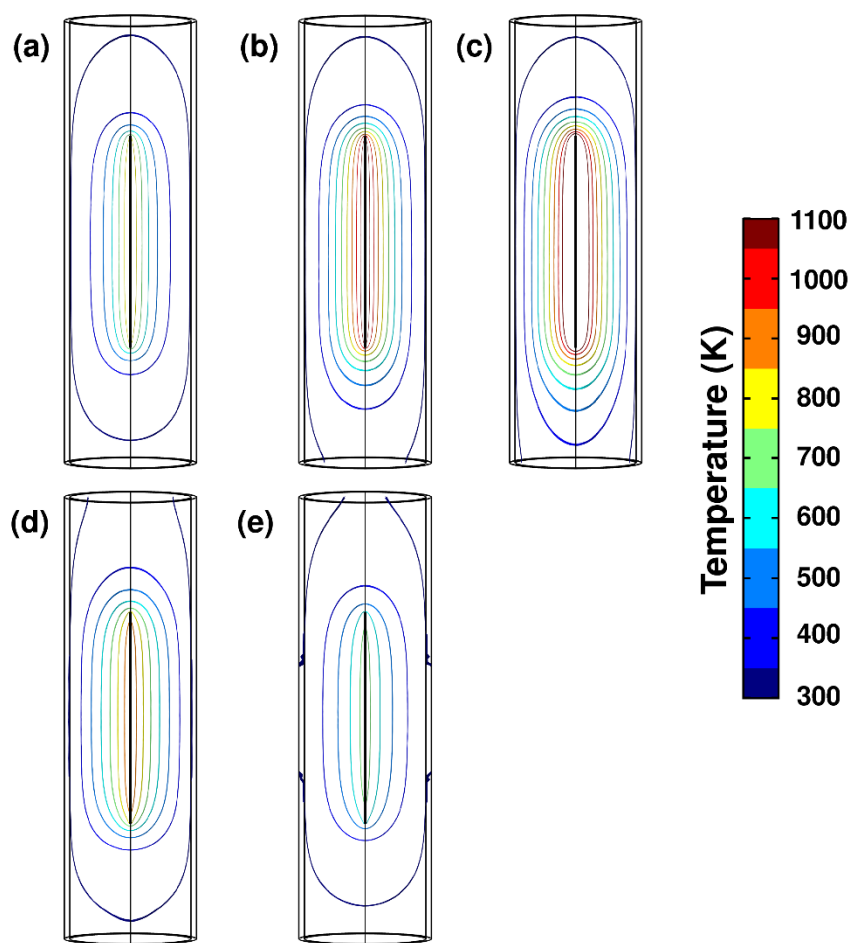


Figure A.11: Temperature contours in the ZX plane at various times of one pulse of 50 V for 50 ms heating and 950 ms cooling with a He inlet flow rate of 90 mL/min. (a) Heating starts, (b) heating in the middle, (c) heating stops, (d) middle of cooling, and (e) cooling stops.

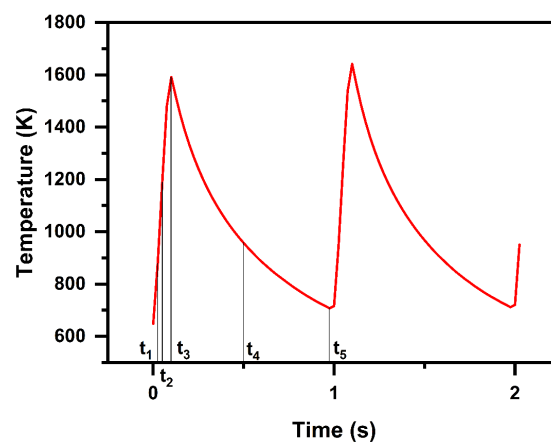


Figure A.12: Temperature profile for 50 V applied for 50 ms and turned off for 950 ms. t_1 = heating starts, t_2 = heating middle, t_3 = heating stops, t_4 = cooling middle, and t_5 = cooling stops.

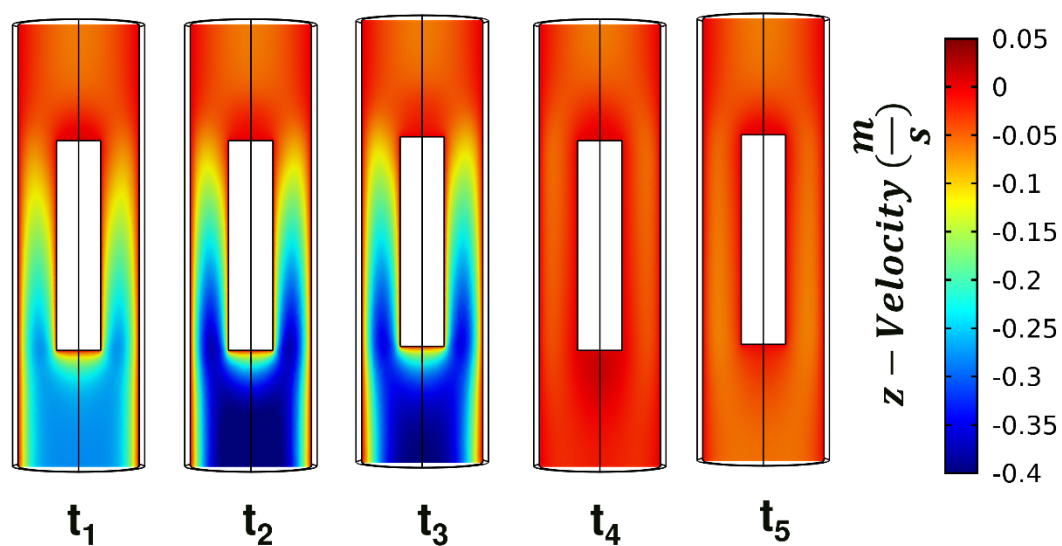


Figure A.13: Axial velocity of He flowing in at 720 mL/min along various times of a pulse of 50 ms of 50 V applied and 950 ms of cooling.

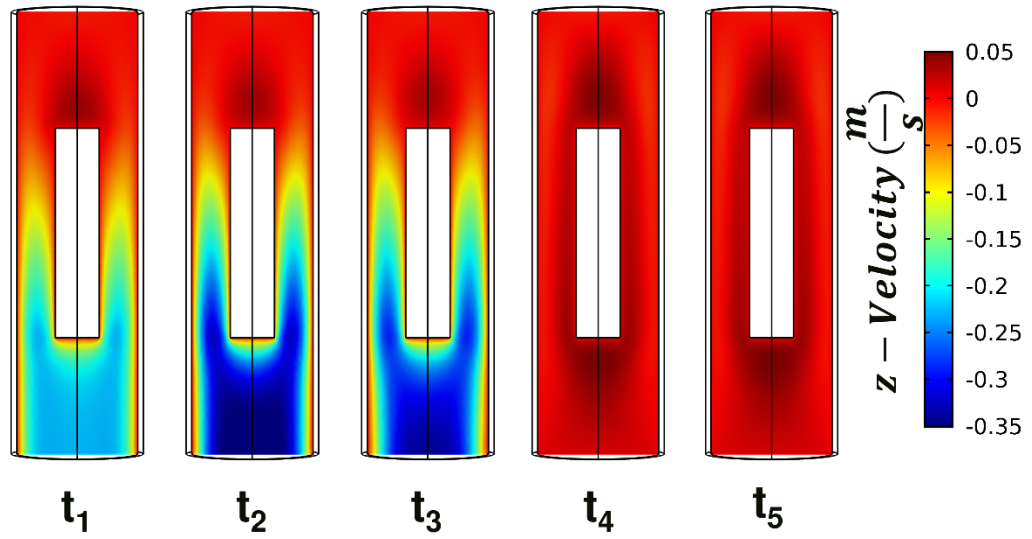


Figure A.14: Axial velocity of He flowing in at 90 mL/min along various times of a pulse of 50 ms of 50 V applied and 950 ms of cooling.

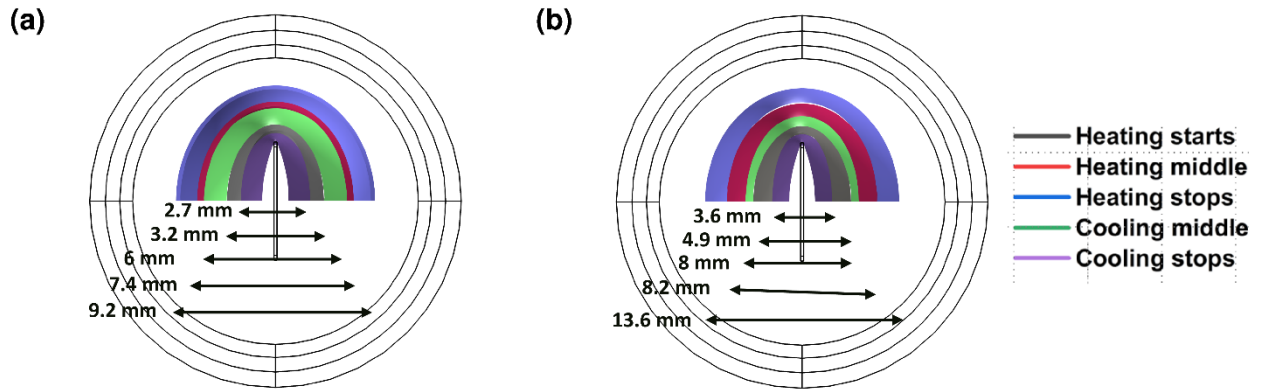


Figure A.15: 600 K isothermal contours at various times of one pulse of 50 V applied for 90 ms and 950 ms of cooling with He flowing at (a) 90 mL/min and (b) 720 mL/min.

Appendix B

JOULE-HEATING MATERIALS FOR ADVANCED CHEMICAL MANUFACTURING

B.1 CFD methods

We solve the electric current, fluid dynamics, and heat-transfer equations. The current density J in the Joule-heating element is described using the Maxwell-Ampere law

$$J = \sigma E + \frac{\partial D}{\partial t} + J_e \quad (\text{B.1})$$

where σ is the electrical conductivity, E is the electrical field intensity, D is the electric displacement, and J_e represents the externally generated current. Eq. B.1 is combined with Eqs. B.2 and B.3.

$$E = -\nabla V \quad (\text{B.2})$$

$$\nabla \cdot J = 0 \quad (\text{B.3})$$

Eq. B.2 defines the electric field, and Eq. B.3 imposes charge conservation. The resistive power density dissipated into a medium, denoted as Q_{eh} , is described as

$$Q_{eh} = \sigma E \cdot E = \sigma \left(\frac{V}{L} \right)^2 = \frac{I \times V}{V_{elem}} = \frac{V^2}{R \times V_{elem}} \quad (\text{B.4})$$

The dissipated power serves as a heat generation term in the energy balance, Eq. B.5

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p U \nabla T = -\nabla(\kappa \nabla T) + Q_{eh} \quad (\text{B.5})$$

Here, T denotes the temperature, ρ is the mass density, C_p is the specific heat, U is the velocity, and κ is the thermal conductivity. The energy balance equation is solved together with Eqs. B.1-B.3, the continuity equation for compressible fluids (Eq. B.6), and the Navier-Stokes equation (Eq. B.7).

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho U) = 0 \quad (\text{B.6})$$

$$\frac{\partial(\rho U)}{\partial t} + \nabla \cdot (\rho U \times U) = \mu \nabla^2 U - \nabla p + \rho g \quad (\text{B.7})$$

In Eq. B.7, μ is the dynamic viscosity and p denotes the pressure.

B.2 Material properties and definitions

B.2.1 Volume to surface area ratio (λ)

A simple energy balance (Eq. B.8-B.10, B.4) can be used to predict the Joule-heating element temperature vs. time for an isothermal element. The energy balance suggests that temperature is also dependent on the geometry of the element.

$$\frac{d(\rho_{elem} C_{p,elem} T_{elem})}{dt} = Q_{eh} - Q_{cc} - Q_{rad} \quad (\text{B.8})$$

$$Q_{cc} = \sum h_i A_i (T_{elem} - T_a) / V_{elem} \quad (\text{B.9})$$

$$Q_{rad} = e \Sigma A (T_{elem}^4 - T_a^4) / V_{elem} \quad (\text{B.10})$$

Here, ρ_{elem} , $C_{p,elem}$, V_{elem} , and T_{elem} represent the density, thermal heat capacity, total volume, and temperature of the element, respectively. Q_{cc} is the heat loss to fluid through conduction and convection. Q_{rad} is the heat loss to the environment via radiation. $\sum h_i A_i$ captures the heat transfer to the carrier gas both via external and internal surface area. T_a is the ambient temperature, assumed to be 20 °C, e is emissivity, and Σ is the Stefan-Boltzmann constant. A is the external surface area of the element. Two volume-to-surface area ratios appear in the energy balance. Because radiative losses dominate the Joule-heated system at high steady-state temperatures, we use $\lambda = V_{elem}/A$. For 3D structures, the ratio $V_{elem}/\sum A_i$ would become significant, requiring further analysis.

B.2.2 Performance metrics

T_{ss} is the spatially averaged steady-state temperature of the Joule-heating element. Steady state is achieved when $\frac{\bar{T}_e(t) - \bar{T}_e(t - \Delta t)}{\bar{T}_e(t - \Delta t)} < 0.001$, where $\bar{T}_e$ is the spatial average temperature over the element volume, and Δt is the time step of integration to t . The value of t when the steady state is achieved is the time to steady state (t_{ss}). The heating rate (R_h) is determined by fitting a linear slope from the initial temperature up to $0.9 * T_{ss}$. The cooling rate (R_c) is calculated similarly, based on the temperature decrease after the power is turned off.

The temperature and current density uniformity of the element at steady state is evaluated using the coefficient of variation (CV).

$$CV (\%) = \frac{Std(x)}{\bar{x}} \times 100 \% \quad (B.11)$$

Here, x is the steady-state temperature or current density at steady state.

B.3 Volume averaging and homogenization

B.3.1 Volume averaging

The governing equations are coarse-grained by applying an averaging operator $\langle \cdot \rangle$ over a length scale l_c as

$$\langle \cdot \rangle = \frac{1}{V_{elem,unit}} \int (\cdot) dV_{elem,unit} \quad (B.12)$$

$V_{elem,unit}$ is the unit cell volume. The effective electrical conductivity is obtained by applying the averaging operator to current conservation at steady state ($J = \sigma E$, Eq. B.1).

$$\sigma_{eff} = \frac{\langle \sigma E \rangle}{\langle E \rangle} = \frac{\langle J \rangle}{\langle E \rangle} \quad (B.13)$$

The local distribution of J and E within the unit cell is obtained using COMSOL and then used to calculate σ_{eff} according to Eq. B.14.

The averaged total volumetric power absorbed is calculated using the methodology as used in *Goyal and Vlachos[132]*. Combined with Eq. B.1 and B.4 gives

$$\langle Q_{eh} \rangle = (1 + \alpha) * \langle J \rangle \cdot \langle E \rangle \quad (B.14)$$

$$(1 + \alpha) = \frac{\langle J \cdot E \rangle}{\langle J \rangle \cdot \langle E \rangle} \quad (B.15)$$

α captures the variation of E at a length scale smaller than l_c within the unit cell. The effective thermal conductivity is also calculated using

$$\kappa_{eff} = \iiint_0^1 \kappa(\xi_1, \xi_2, \xi_3) \frac{\partial T}{\partial \xi_1} d\xi_1 d\xi_2 d\xi_3 \quad (B.16)$$

Here, κ is the thermal conductivity function of space, ξ_i are the fast variables defined as $\xi_i = x_i/l_i$, x_i being the spatial coordinates and with l_i being the length of the unit cell with $i = 1, 2$, and 3.

B.3.2 Unit cell calculation

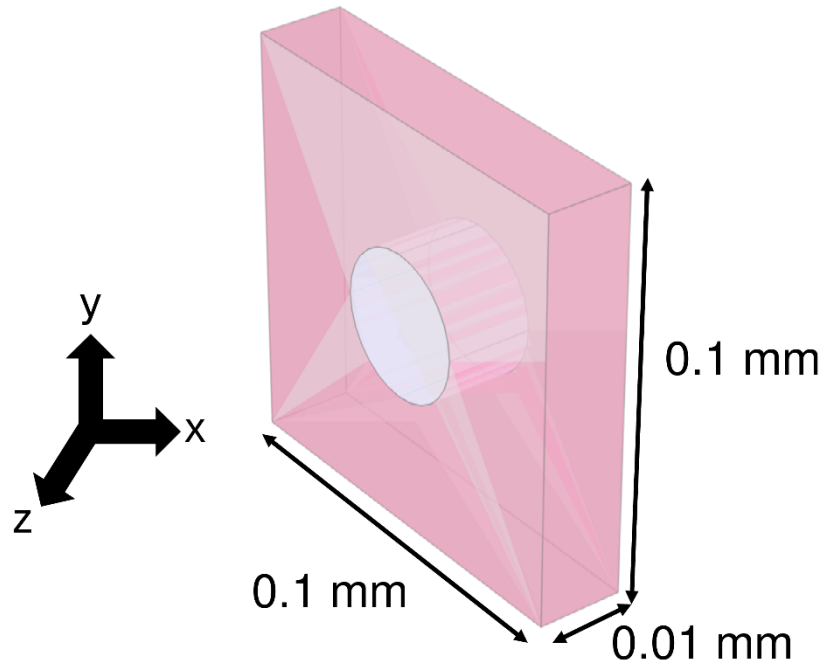


Figure B.1: Square unit cell with variable cylindrical pore size. Edge length = 0.1 mm and cell thickness = 0.01 mm.

We assume a square unit cell containing a cylindrical pore of variable radius. The unit cell material is the same as the Joule-heating element, while He is chosen to represent the pore. The unit cell is modeled in COMSOL. For the calculations of σ_{eff} and $\langle Q_{eh} \rangle$, a fixed voltage difference is applied across the unit cell, with the top edge

set to $V = V_0$ and the bottom-edge to $V = 0$. All other faces are assumed to be thermally and electrically insulated. Eqs. B.1- B.5 are solved using COMSOL for this geometry.

B.4 Parametric analysis

B.4.1 Fitting Statistics

Table B.1: R^2 value in power law model.

R^2 value	Heating rate	Cooling rate	Time to steady-state	Steady-state Temperature
Density	0.93	0.97	0.93	0.93
Heat Capacity	0.93	0.97	0.97	0.93
Electrical Conductivity	0.88	-	0.91	0.9
Voltage	0.92	-	0.98	0.92
Length	0.99	-	0.97	0.97
Thickness	0.96	0.89	0.91	0.9
Emissivity	0.94	0.97	0.8	0.85

B.4.2 Fitted equation performance

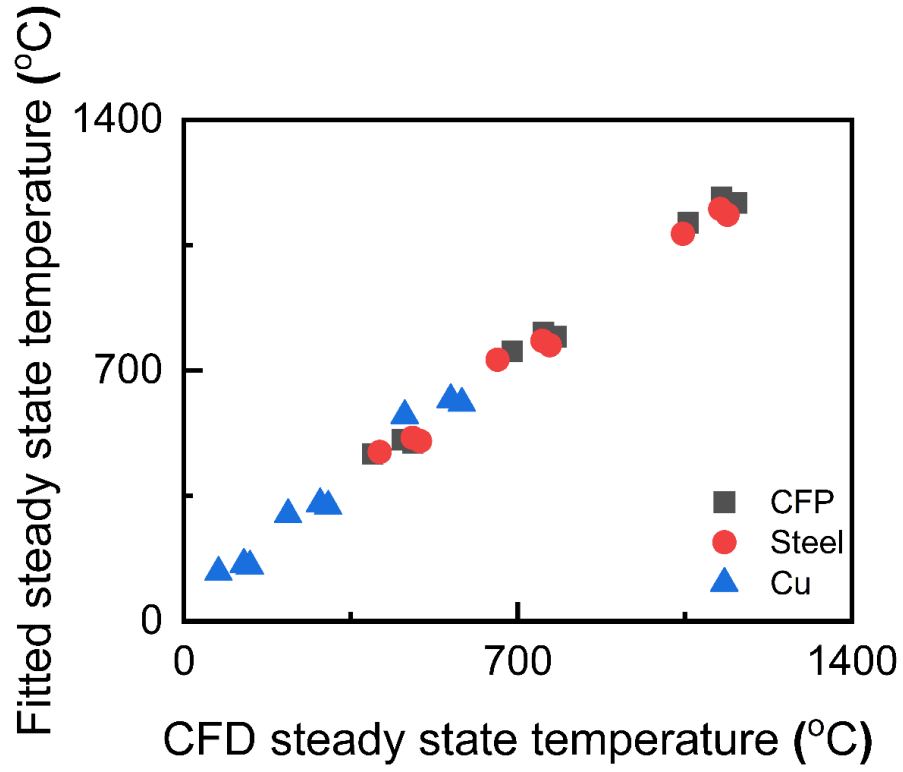


Figure B.2: Comparison of the fitted expression (Eq. 3.3) and CFD-calculated steady-state temperatures for three materials: copper, stainless steel, and carbon fiber paper (CFP). Simulations are performed with $L = 38$ mm, $\lambda = 0.2$ mm, and V ranging from 5 to 30 V.

B.5 Critical thermal conductivity

B.5.1 Parametric analysis of temperature uniformity

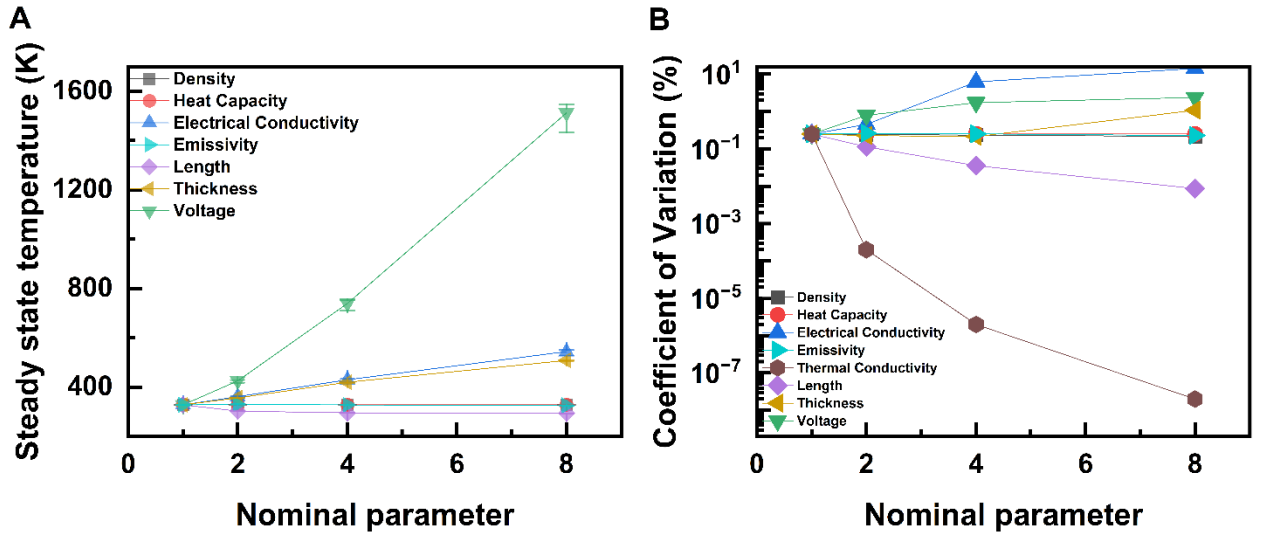


Figure B.3: Parametric analysis and quantification of temperature uniformity. (a) Parametric analysis of the steady-state temperature (top error bar = maximum element temperature, lower error bar = minimum element temperature, point = volumetric average temperature of element). (b) Parametric analysis of temperature non-uniformity and ΔT for a scaling factor = 8 ($\Delta T = T_{max} - T_{min}$). Nominal parameters ($L = 38$ mm, thickness = 0.0525 mm, Voltage = 3.75 V, emissivity = 0.123125, material properties same as those of the carbon fiber).

B.5.2 Energy balance over the element

Energy conservation equation in rectangular coordinates for a solid is

$$\frac{\partial T}{\partial t} = \left(\frac{1}{\rho C_p} \right) \left[\kappa_1 \frac{\partial^2 T}{\partial x_1^2} + \kappa_2 \frac{\partial^2 T}{\partial x_2^2} + \kappa_3 \frac{\partial^2 T}{\partial x_3^2} \right] + \frac{H_V}{\rho C_p} \quad (\text{B.17})$$

Here, H_V is the energy source term density and κ_i is the thermal conductivity of the element in the direction i . For a Joule-heating element at steady state (left-hand side = 0), this can be simplified to ($H_V = Q_{eh} = \sigma E \cdot E$. After assuming constant σ across the element's volume, $\sigma E \cdot E = \sigma \left(\frac{V}{L} \right)^2$)

$$\kappa_1 \frac{\partial^2 T}{\partial x_1^2} + \kappa_2 \frac{\partial^2 T}{\partial x_2^2} + \kappa_3 \frac{\partial^2 T}{\partial x_3^2} = -\sigma \left(\frac{V}{L} \right)^2 \quad (\text{B.18})$$

$$-\kappa_i \frac{\partial T}{\partial x_i} = h_{ti}(T - T_a) \text{ at } x_i = 0 \text{ and } L_i \quad (\text{B.19})$$

L_i represents the element length along direction i . h_{ti} represents the total heat transfer coefficient in direction i . This equation in dimensionless form is

$$\sum_i \kappa_i \frac{\partial^2 \theta}{\partial \zeta_i^2} = -\frac{\sigma \left(\frac{V}{L} \right)^2 L_i^2}{T_a} \quad (\text{B.20})$$

$$\frac{\partial \theta}{\partial \zeta_i} = -\frac{h_{ti} L_i (\theta - 1)}{\kappa_i} \text{ at } \zeta_i = 0 \text{ and } 1 \quad (\text{B.21})$$

$$\zeta_i = x_i / L_i \quad (\text{B.22})$$

$$\theta = T / T_a \quad (\text{B.23})$$

For the element volume and surface to remain isothermal, $\frac{\partial \theta}{\partial \varsigma_i}$ and $\frac{\partial^2 \theta}{\partial \varsigma_i^2}$ should tend to zero. This implies the magnitude of the right-hand side (RHS) of Eqs. B.21- B.22 should tend to zero. Since the RHS depends on L_i and κ_i , we consider the dimension with the largest L_i/κ_i (for isotropic materials, this is the longest dimension). Eqs. B.21 and B.22 give Eqs. B.25-B.26.

$$\frac{\sigma V^2}{\kappa * T_a} \ll 1 \quad (\text{B.24})$$

$$\frac{Bi h_t}{h} \ll 1 \quad (\text{B.25})$$

$$Bi = \frac{hL}{\kappa} \quad (\text{B.26})$$

Eq. B.25 captures the dynamics between resistive heat generation and internal conduction, with the LHS typically having a magnitude on the order of $O(10^{-1})$ to $O(10^1)$. In contrast, Eq. B.26 captures the dynamics between heat losses to the carrier gas and internal conduction, with the LHS magnitude typically ranging from $O(10^{-2})$ to $O(1)$. As reported in the literature,[[75, 117]] heat losses primarily govern isothermicity, and a near-zero value of $\frac{\partial \theta}{\partial \varsigma_i}$ implies a near-zero value of $\frac{\partial^2 \theta}{\partial \varsigma_i^2}$.

Therefore, Eq. B.26 is sufficient for isothermicity. Based on our assumptions, $Bi < 0.01$ (a typical value in asymptotics) ensures isothermicity. Combining this with the Bi definition using the Nu number, we obtain the expression for κ_{crit} .

$$Bi = Nu \times \left(\frac{\kappa_g}{\kappa} \right) \quad (\text{B.27})$$

$$\kappa_{crit} = \frac{Nu\kappa_g}{\varepsilon} \quad (\text{B.28})$$

Here $\varepsilon \ll 1$ to satisfy Eq. B.26. Critical thermal conductivity for various geometries can be calculated from Eq. B.29, combined with the empirical correlation of Nu from the literature. For brevity, we discuss only a vertical heating tape.

$$\kappa_{crit} = 100 \times \left(0.68 + \frac{0.663Ra_L^{0.25}}{\left(1 + \left(\frac{0.492}{Pr} \right)^{\frac{9}{16}} \right)^{\frac{4}{9}}} \right) \times \kappa_g \quad (\text{B.29})$$

$$Ra_L = \frac{\rho_g^2 C_{p,g} \Delta T L^3 g}{T \mu \kappa_g} \quad (\text{B.30})$$

$$Pr = \frac{C_{p,g} \mu}{\kappa_g} \quad (\text{B.31})$$

Eq. B.30 can be simplified using Eq. B.31-B.32, and approximate scaling relations can be derived

$$\kappa_{crit} \propto L^{0.75} \rho_g^{0.5} C_{p,g}^{0.5} \kappa_g^{0.5} \quad (\text{B.32})$$

Figure B.4 shows the variation of κ_{crit} with temperature for the nominal tape conditions.

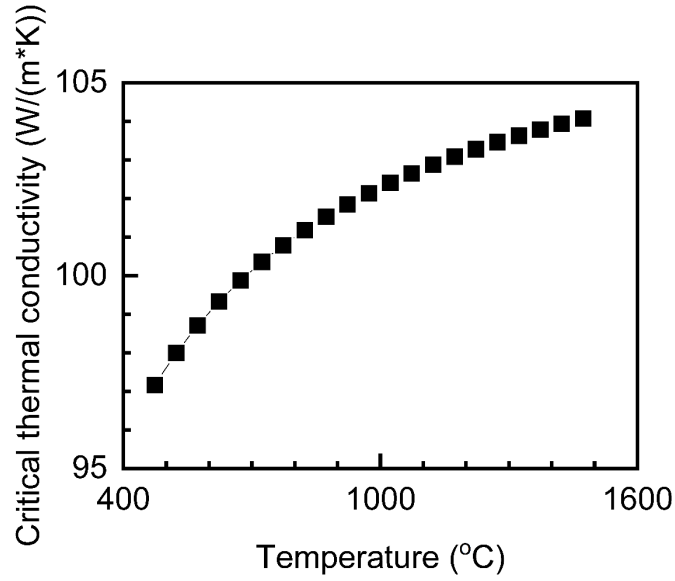


Figure B.4: Critical thermal conductivity of a vertical heating tape (Eq. B.32) element for *He* as the carrier gas vs. temperature of the tape.

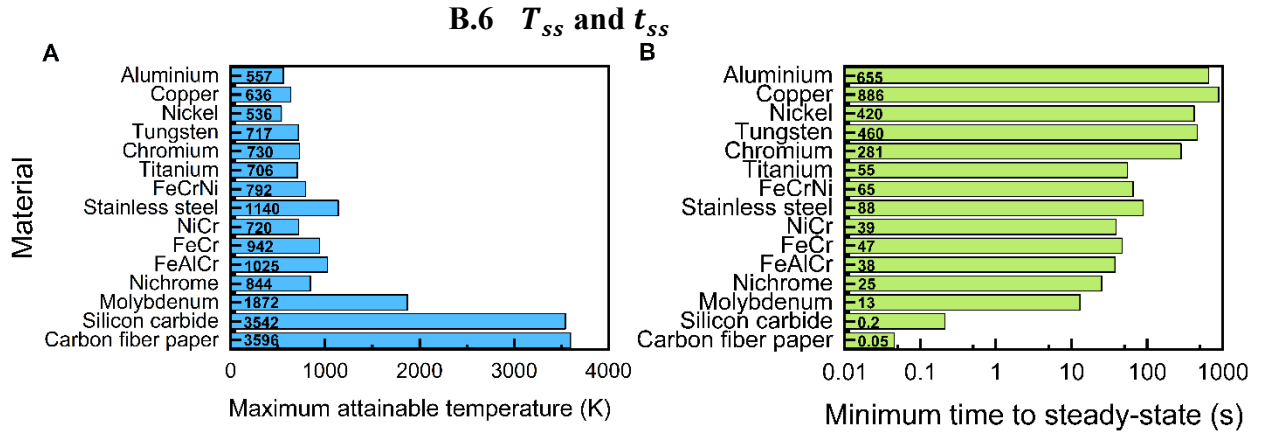


Figure B.5: Maximum attainable temperature and minimum time to steady-state for fixed $\lambda = 0.1$ mm for various materials.

While the maximum heating rate is dictated by material properties, the maximum steady-state temperature and the minimum time to reach steady state are influenced by the volume-to-surface area ratio (λ).

$$\text{Maximum steady state temperature (K): } T_{ss,limit} = \frac{\lambda J_{max}^2 L}{\sigma} \quad (\text{B.33})$$

$$\text{Minimum time to steady state (s): } t_{ss,limit} = \frac{\rho C_p \lambda \sigma}{J_{max}} \quad (\text{B.34})$$

As λ increases, both the maximum steady-state temperature and minimum time to steady-state also increase (Eq. B.34-B.35). Figure B.6 demonstrates that for an element with a volume-to-surface area ratio of 0.1 mm, carbon-based materials achieve three times higher steady-state temperatures and two orders of magnitude shorter times to steady-state than alloys.

Table B.2: Voltage required to reach the maximum heating rate for each material.

Material	Maximum voltage (V/m)
CFP	4950.5
SiC	5659.3
FeAlCr	14.0
Nichrome	15.0
Stainless steel	7.1
Chromium	1.2
Molybdenum	52.0
Tungsten	0.6
Copper	0.3
Aluminum	0.3
Titanium	4.2
Nickel	0.7
FeCr	10.0
FeCrNi	6.7
NiCr	9.1

B.7 Machine learning on material properties

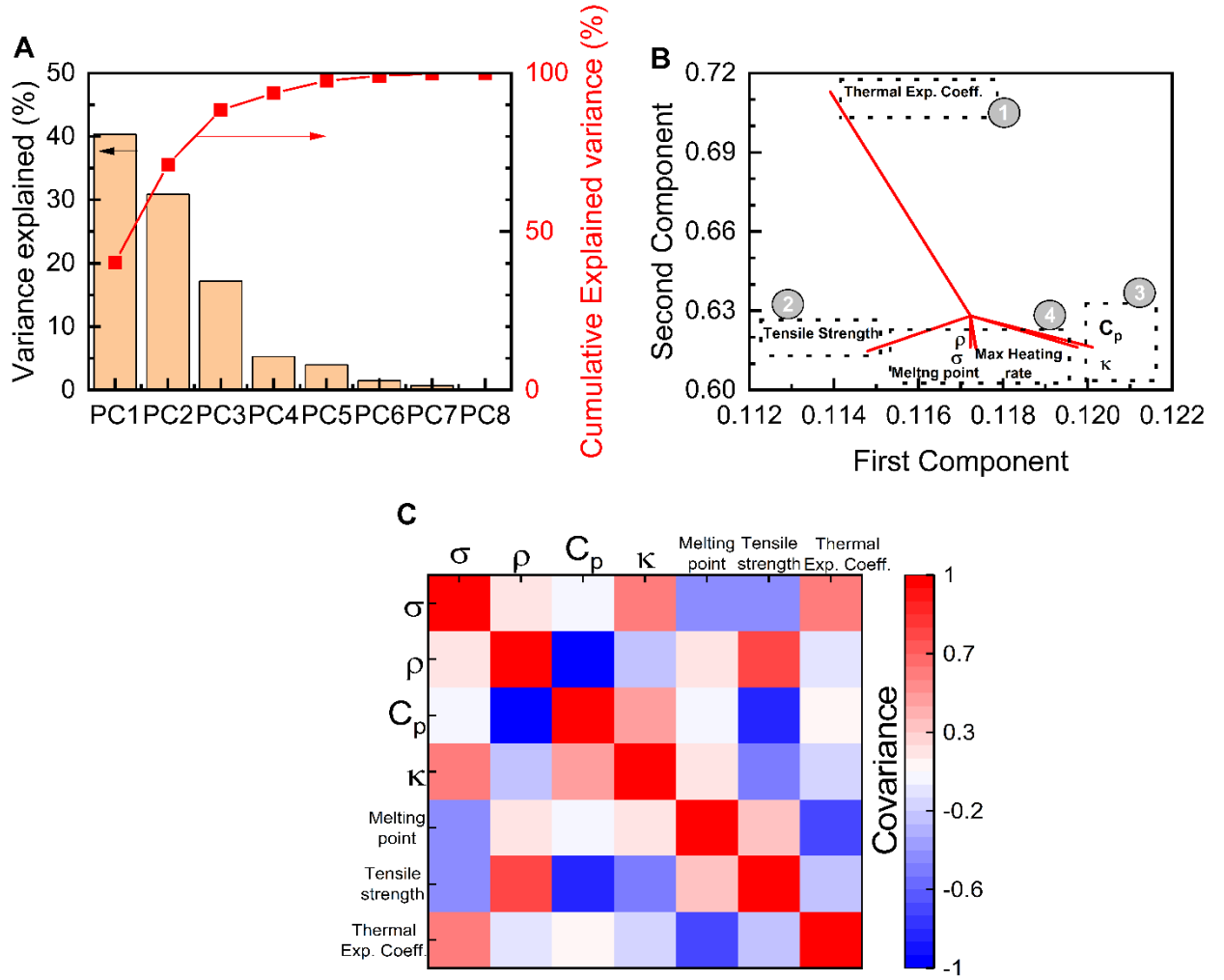


Figure B.6: Interdependency of intrinsic material properties (Table B.1). (A) PCA on material properties. (B) Properties projection on principal component plane. The numbers shown are the group numbers discussed in the MS. (C) Covariance matrix, which shows material properties' interdependency. Red means directly correlated, and blue means inversely correlated.

B.8 Material selection flow diagram

Equation B.8 calculates the power density required to maintain the steady-state temperature, as shown in Eq. B.36. Equation B.36 can be further simplified to Eq. B.37 by assuming negligible power loss to the fluid. Here T_{op} is the operating temperature. This assumption holds for preheated carrier gases and systems operating at high temperatures. A general range of values is shown in Figure B.7.

$$\text{Power density required to maintain steady state: } P_{ss} \left(\frac{W}{cm^3} \right) : Q_{cc} + Q_{rad} \quad (B.35)$$

$$P_{ss} \sim e\Sigma(T_{op}^4 - T_a^4)/\lambda \quad (B.36)$$

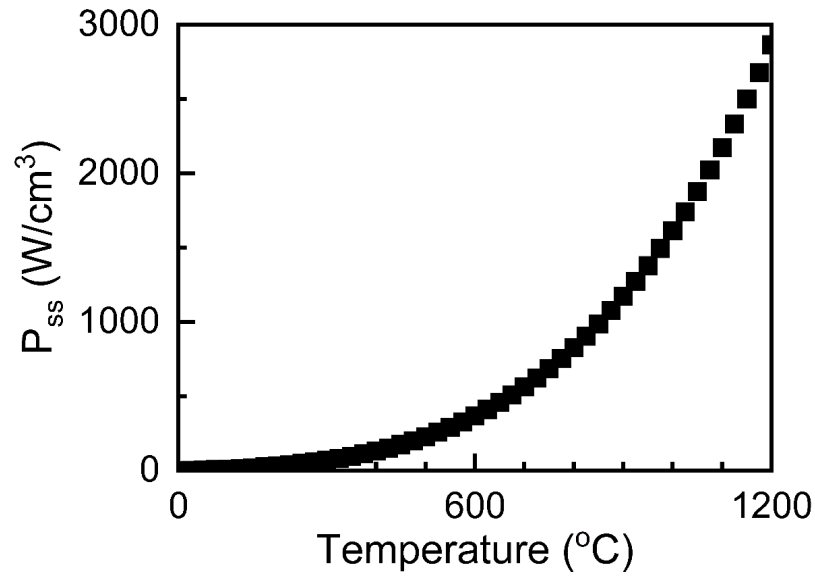


Figure B.7: Power density required to maintain steady-state temperature (Eq. B.36) across a range of operating temperatures ($e=1$ and $\lambda = 0.1 \text{ mm}$).

B.9 Porous elements results

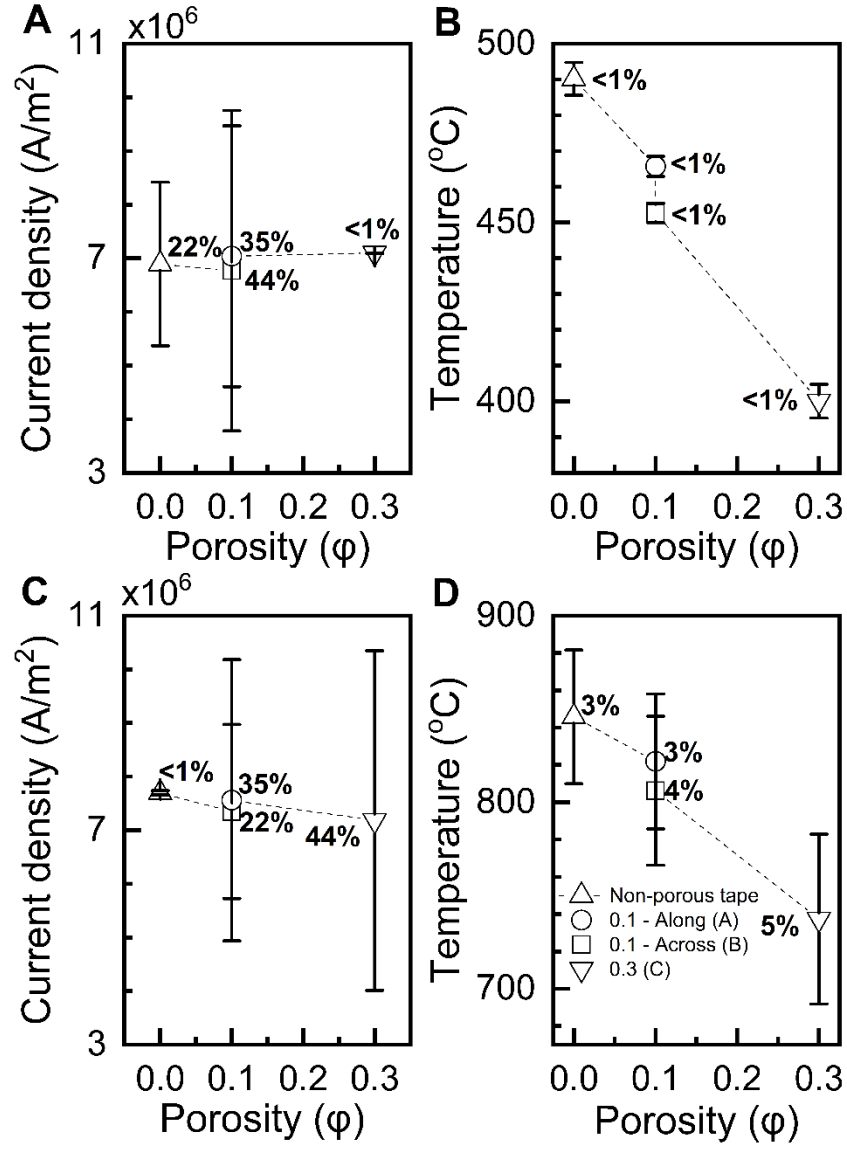


Figure B.8: Porosity-specific volume-averaged current density (A) and temperature (B) for copper. Porosity-specific volume-averaged current density (C) and temperature (D) for stainless steel. The numbers represent the CV, and the bars indicate the variance across the volume.

The sudden drop in the coefficient of variation (CV) of electric current density in copper when porosity increases from 0.2 to 0.3 occurs due to an increase in electrical conductivity, which results from the corresponding decrease in temperature.

B.10 Effective properties

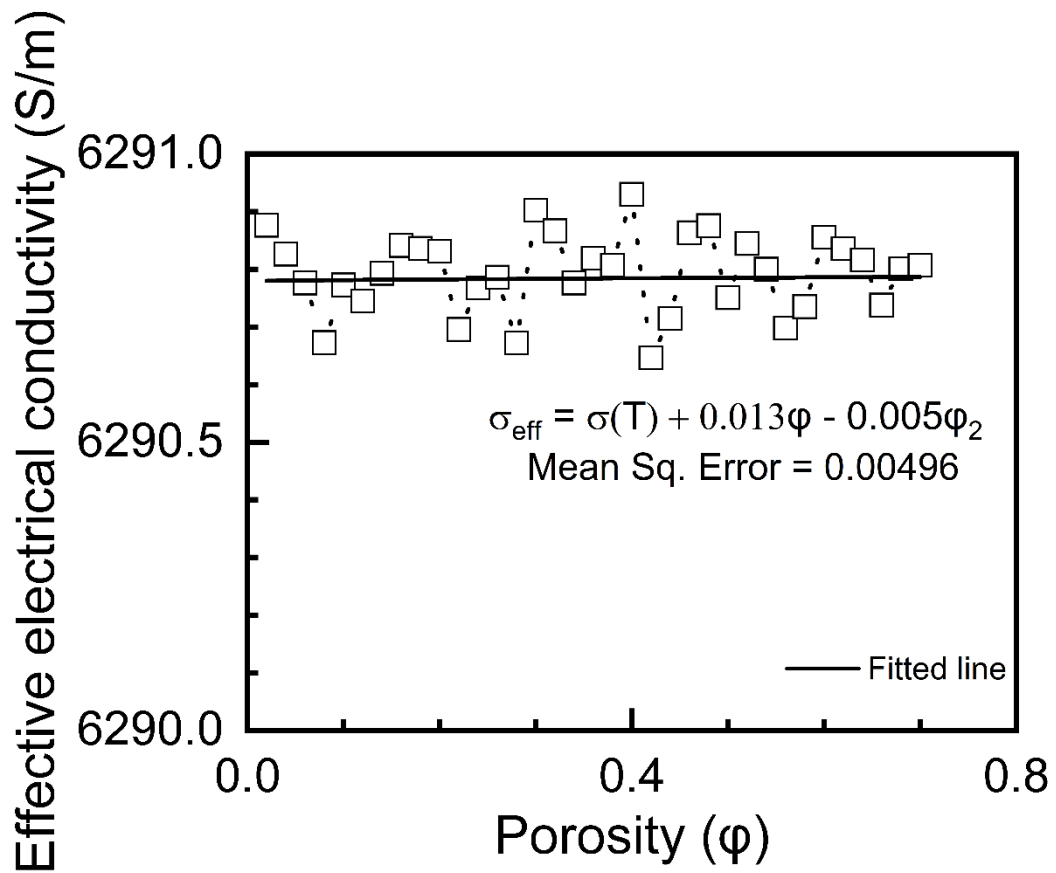


Figure B.9: Effective electrical conductivity calculated for varying porosity, assuming CFP unit cell at 20°C. The expression shows the fitted expression.

Effective electrical conductivity increases slightly with increasing porosity; however, this change is minimal. Effective electrical conductivity is weakly dependent on porosity.

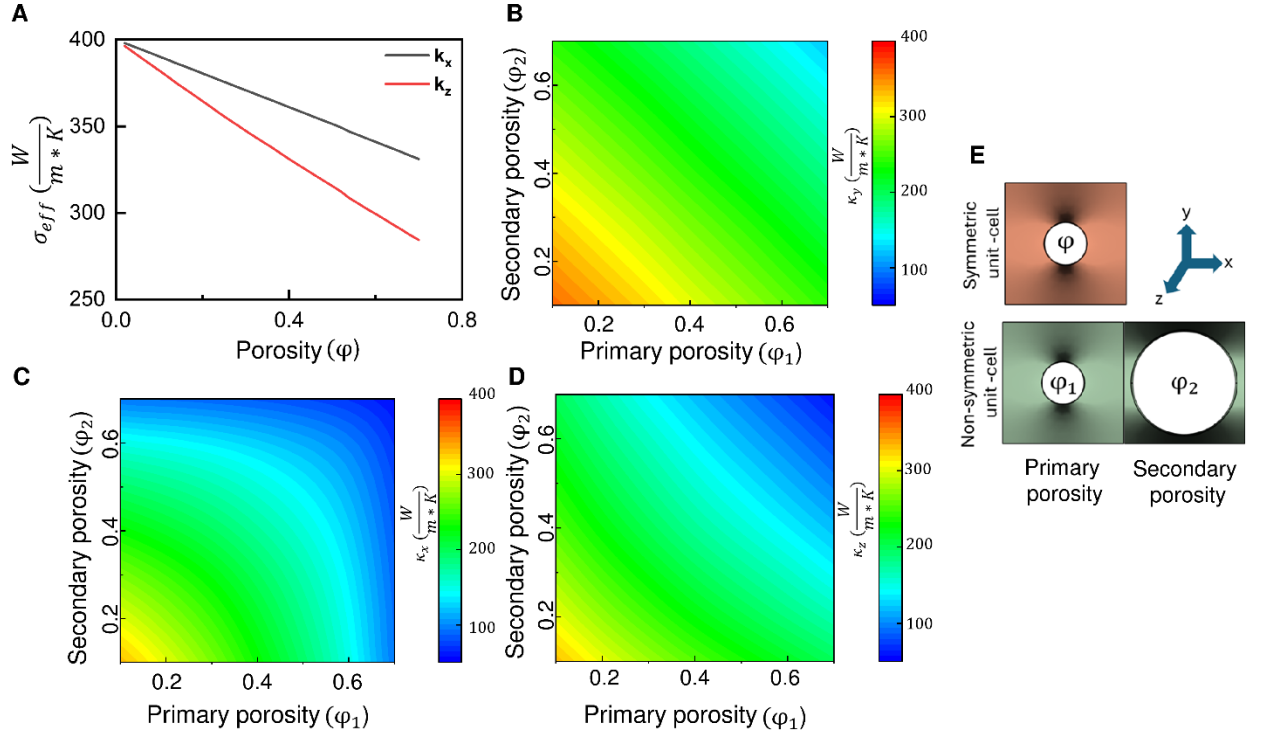


Figure B.10: Effective thermal conductivity of carbon fiber unit cells. (A) Symmetric unit cell with uniform porosity. (B–D) Thermal conductivity along the y-, x-, and z-axes, respectively, for asymmetric unit cells with two pore sizes. (E) Schematic illustrating pore placement and axis orientation in each unit cell configuration.

Appendix C

SHORT CONTACT TIME, HIGH TEMPERATURE, INTERNALLY-HEATED ETHANE CRACKERS

C.1 Lumped Kinetic Model

Table C.1: Lumped kinetic scheme for C₂H₆ cracking.

No.	Reactions	Pre-exponential Constant (s ⁻¹) or ^b (cm ³ mol ⁻¹ s ⁻¹)	Activation Energy (kJ mol ⁻¹)
1	$C_2H_6 \leftrightarrow C_2H_4 + H_2$	4.6×10^{13}	272.8
2	$C_3H_6 \leftrightarrow C_2H_2 + CH_4$	7.2×10^{12}	274.2
3	$C_2H_2 + C_2H_4 \rightarrow C_4H_6$	$1.0 \times 10^{15} \text{ }^b$	172.6
4	$C_2H_4 + C_4H_6 \rightarrow C_6H_6 + 2H_2$	$8.3 \times 10^{12} \text{ }^b$	144.6
5	$C_3H_8 \leftrightarrow C_3H_6 + H_2$	5.8×10^{10}	214.6
6	$C_3H_8 + C_2H_4 \rightarrow C_2H_6 + C_3H_6$	$2.5 \times 10^{16} \text{ }^b$	247.1
7	$C_3H_6 \rightarrow 1.5C_2H_4$	7.3×10^{12}	268.5
8	$C_2H_6 \rightarrow 0.5C_3H_8 + 0.5CH_4$	3.8×10^{11}	273.0
9	$C_4H_{10} \leftrightarrow C_4H_8 + H_2$	1.6×10^{12}	260.9
10	$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$	$7.0 \times 10^{16} \text{ }^b$	252.8
11	$C_3H_6 + C_2H_6 \rightarrow C_4H_8 + CH_4$	$1.0 \times 10^{17} \text{ }^b$	251.1

Table C.2: Reverse reaction rate constants.

No.	Pre-exponential Constant ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Activation Energy (kJ mol^{-1})
1	8.49×10^{11}	136.5
2	3.81×10^{11}	147.2
5	9.03×10^8	93.5
9	1.78×10^{10}	135.1

To identify the optimal operating window for C_2H_6 cracking, we utilized an isothermal plug flow reactor (PFR) model in the reaction engineering module of COMSOL Multiphysics software, referenced hereafter as COMSOL. The model incorporates the kinetics proposed by *Ranjan et al.* (Table C.1 and Table C.2),[113] which predicts the formation of higher-molecular-weight species under industrial conditions. Steam in the feed is treated as an inert diluent; reactions involving steam and coke are not included.

In parallel, a 3D continuous flow Joule-heated reactor was modeled in COMSOL. The model contains a quartz tube reactor (length (L_r) = 360 mm, ID ($2 \times r$) = 22 mm) containing a thin, long CFP (length (L) = 38 mm, width (L_w) = 8 mm, and thickness (L_{th}) = 0.21 mm. The model solves the coupled fluid dynamics, heat transfer, species transport, and C_2H_6 cracking kinetics using COMSOL's heat transfer, transport of concentrated species, chemistry, and laminar flow modules. The model solves the continuity equation for compressible fluids (Eq. C.1), and the Navier-Stokes Equation (Eq. C.2).

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho U) = 0 \quad (\text{C.1})$$

$$\frac{\partial(\rho U)}{\partial t} + \nabla \cdot (\rho U \times U) = \mu \nabla^2 U - \nabla p + \rho g \quad (C.2)$$

Here, ρ is the mass density, U is the velocity, μ is the dynamic viscosity, and p denotes the pressure. Eqs. C.1-C.2 are solved together with the energy balance equation (Eq. C.3).

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p U \nabla T = -\nabla(\kappa \nabla T) + Q \quad (C.3)$$

In Eq. C.3, T denotes the temperature, C_p is the specific heat, κ is the thermal conductivity, and Q is the heat of reaction. Mass transport is implemented by

$$\nabla \cdot j_i + \rho(U \cdot \nabla)\omega_i = R_i \quad (C.4)$$

Here, ω_i is the mass fraction of species i , j_i is the mass flux vector, and R_i is the rate expression for consumption or production. The mass flux is defined as

$$j_i = -\rho D_i^m \nabla \omega_i - \rho \omega_i D_i^m \frac{\nabla M_n}{M_n} + \rho \omega_i \sum_k \frac{M_i}{M_n} D_k^m \nabla x_k \quad (C.5)$$

$$D_i^m = \frac{1 - \omega_i}{\sum_{k \neq i} \frac{x_k}{D_{ik}}} \quad (C.6)$$

$$M_n = \left(\sum_i \frac{\omega_i}{M_i} \right)^{-1} \quad (C.7)$$

Here, D_i^m is the averaged molecular diffusion of species i , M_n is the mixture-averaged mass, x_k is the mole fraction, D_{ik} is the binary diffusion coefficient (calculated using Chapman-Enskog kinetic gas theory), and M_i is the molecular mass of species i .

A stepwise steady-state simulation strategy was implemented to improve convergence. In Step 1, the heat transfer, laminar flow, and chemistry modules were solved. Step 2 incorporated species transport, solving the chemistry, laminar flow, and transport modules using results from Step 1. In Step 3, all physics interfaces were solved simultaneously using the output from Step 2 as the initial condition. This multi-step approach improved convergence by incrementally refining the solution.

The boundary conditions are the same as in previous work, with modifications.[1] The CFP surfaces are assumed to be at constant operating temperature. The inflow consisted of 5-70 mol% C₂H₆ gas diluted in He at 20 °C. The total inlet flow rate was 50-300 standard cubic centimeters per minute (sccm). NASA polynomials were utilized to calculate C_p of all species. In-built mixture-averaged expressions were utilized to calculate the mixture-averaged C_p , κ , and μ . A mesh dependency was performed to ensure discretization-independent results. We utilized a fine general physics mesh for the heating CFP and a normal mesh for the quartz tube and the fluid dynamics.

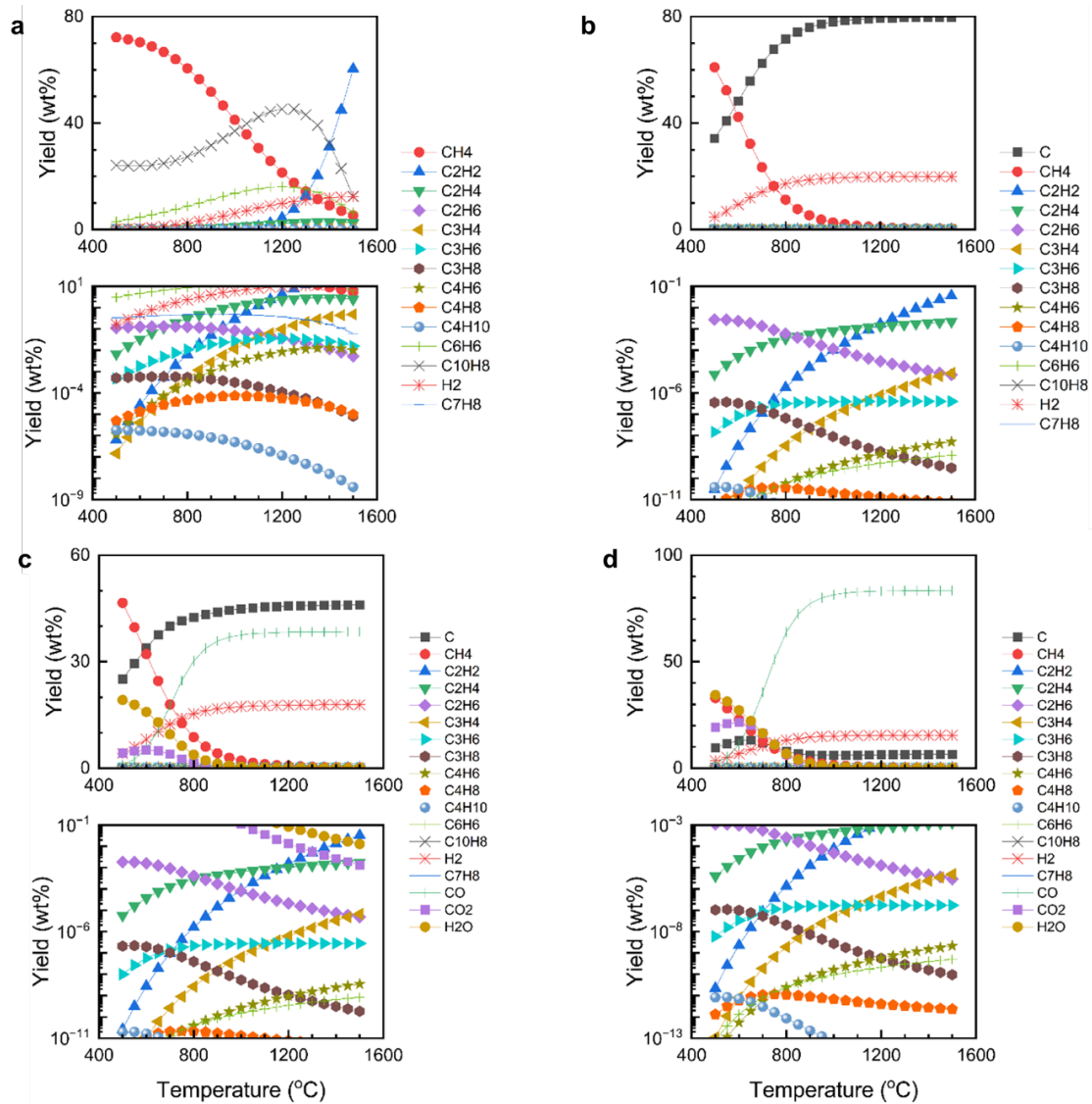


Figure C.1: Equilibrium data. (a) Without coke included (undiluted, 1 atm), (b) with coke (undiluted, 1 atm), (c) 0.3 kg_{steam}/ kg_{C₂H₆}, and (d) 1 kg_{steam}/ kg_{C₂H₆}. Steam dilution minimizes coking, and the higher the dilution, the less the coke at higher temperatures. A lower ethane partial pressure reduces bimolecular reactions, enhancing $Y_{C_2H_4}$. Calculation performed using the ThermoSolver.[112]

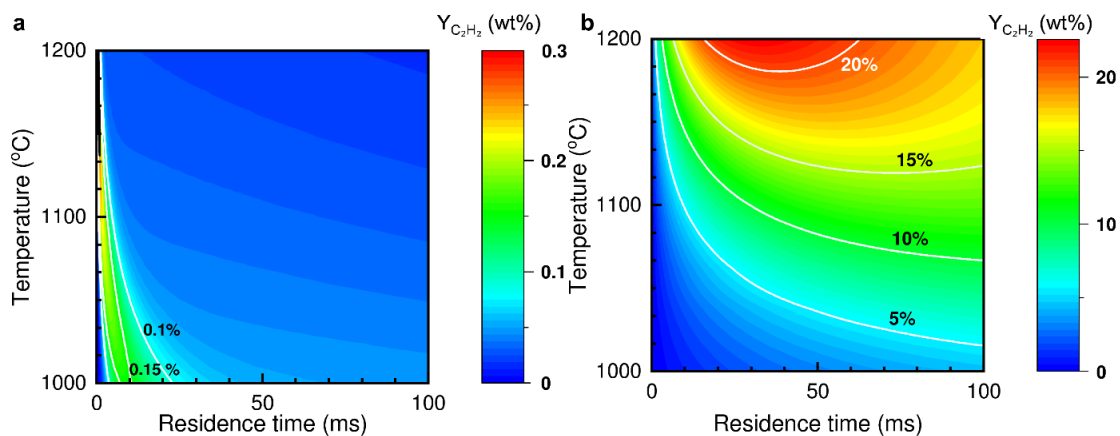


Figure C.2: Predicted $Y_{C_2H_2}$ performance maps (PFR, dry basis data, Feed: 70 mol% C_2H_6 and 30 mol% He and 1 atm). $Y_{C_2H_2}$ predicted using (a) lumped kinetic model and (b) the detailed microkinetic model. The numbers represent iso-contour values.

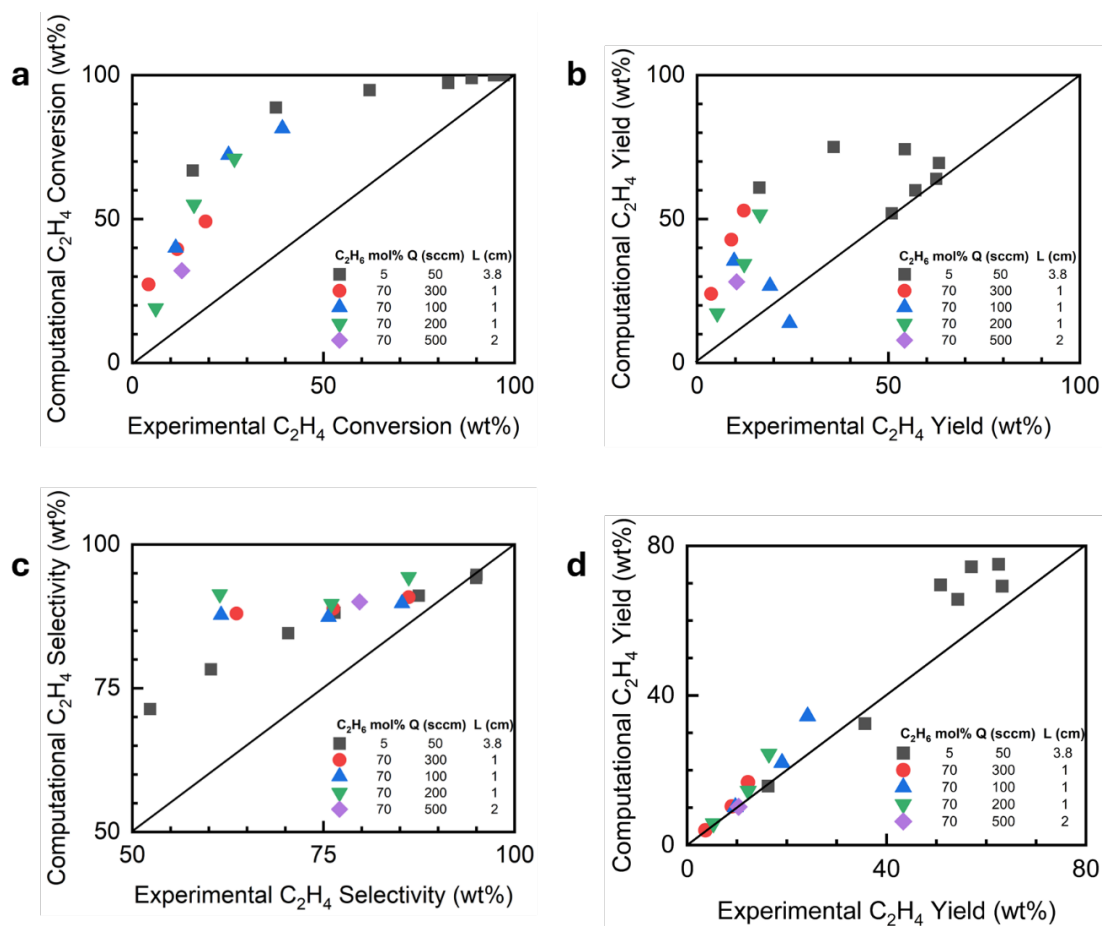


Figure C.3: CFD prediction of the CFP Joule-heated reactor using the original kinetic model.[113] Parity plots of predicted vs. experimental data for (a) $X_{C_2H_6}$, (b) $Y_{C_2H_4}$, (c) $S_{C_2H_4}$ for the same temperature and total flow rate, and (d) $S_{C_2H_4}$ at similar conversion. All data are reported on a dry basis. $RMSE(X_{C_2H_6}) = 0.2$.

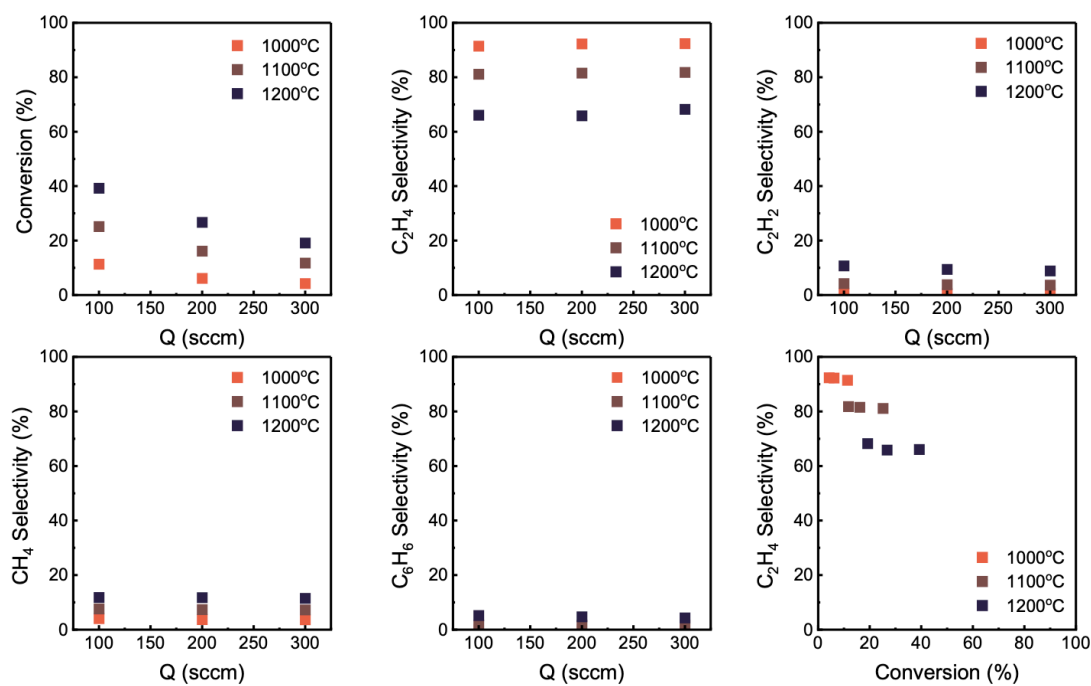


Figure C.4: Experimental data of thermal C_2H_6 cracking in CJH. $X_{C_2H_6}$ vs. flowrate, carbon-atom-based selectivity ($S_{C_2H_4}$, $S_{C_2H_2}$, S_{CH_4} , $S_{C_6H_6}$) vs. flowrate, $S_{C_2H_4}$ vs. $X_{C_2H_6}$. Experiments at atmospheric pressure with 70 mol% C_2H_6 with He balance, 100 – 300 sccm flow rate, 1000 – 1200 °C, and a $10 \times 8 \times 0.21$ mm³ CFP heating element. All data are reported on a dry basis.

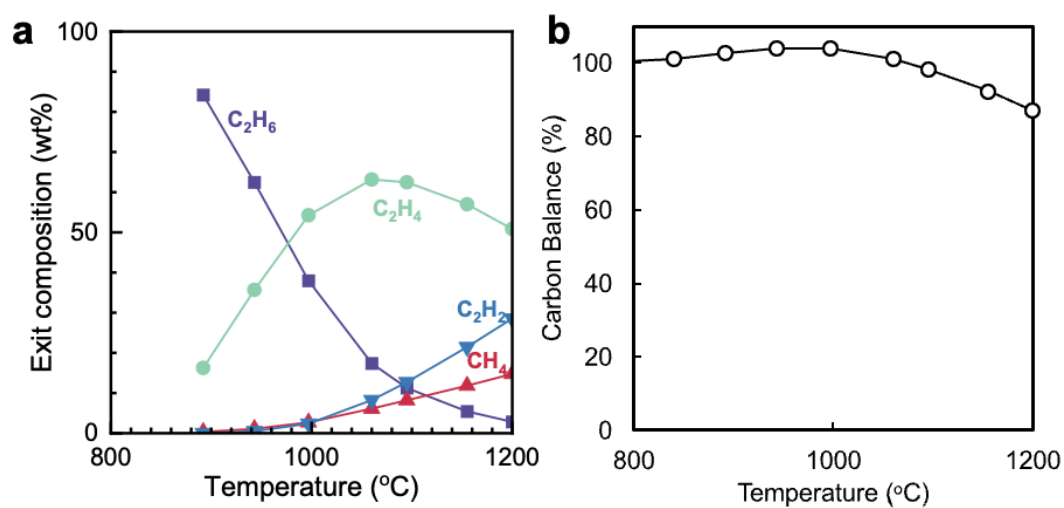


Figure C.5: Experimental data of diluted thermal C_2H_6 cracking in CJH. (a) Experimental exit composition vs. temperature, for 50 sccm and 5 mol% C_2H_6 feed (balance He). (b) Carbon balance over temperature. Experiments at atmospheric pressure with CFP of $L = 3.8$ cm. All data are reported on a dry basis.

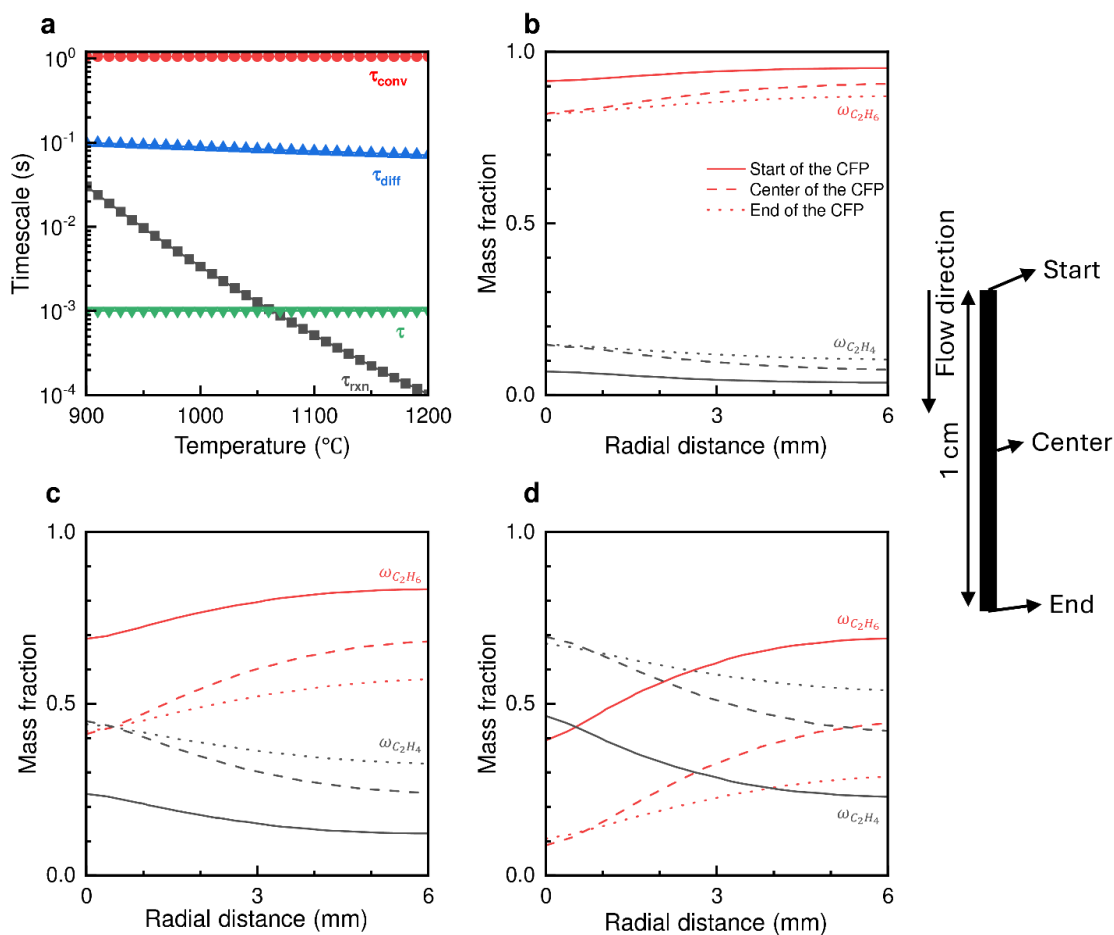


Figure C.6: Transport timescale analysis of ethane cracking using CFP. Feed: 70 mol% ethane (balance He), $L = 1$ cm, and $Q = 100$ sccm. (a) Reaction ($\tau_{rxn} = 1/k_{C_2H_6 \rightarrow C_2H_4 + H_2}$; reaction rate parameters taken from Table C.1), diffusion ($\tau_{diff} = r^2/D_{C_2H_6,He}$), convection ($\tau_{conv} = L/u$), and residence timescale ($\tau = V_{elem}/Q$) vs. temperature. CFD predicted mass fraction of ethane and ethylene around the CFP at (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C. All data are reported on a dry basis.

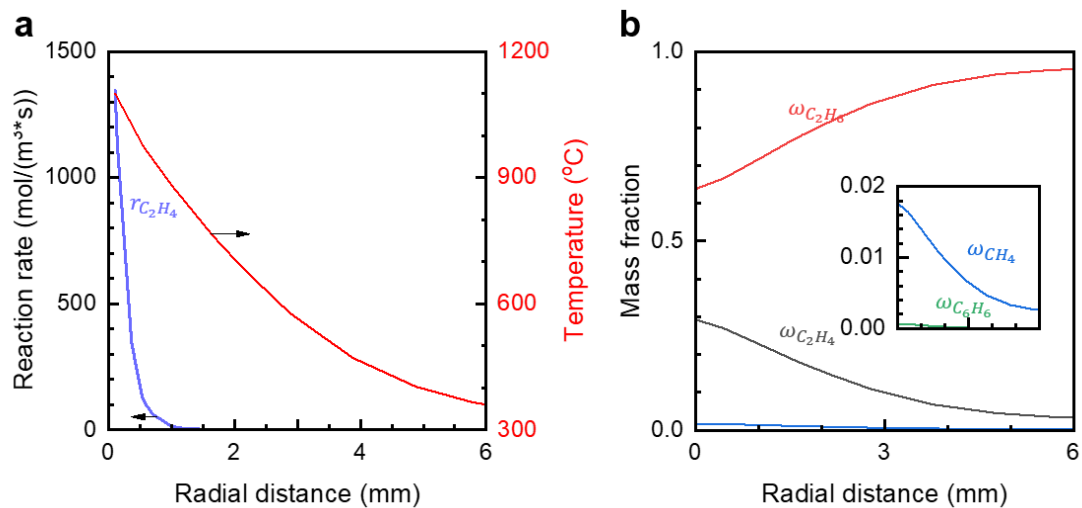


Figure C.7: Radial data in the center of the CFP Joule-heated reactor at 1100 $^{\circ}\text{C}$ with $L = 1$ cm and total flow rate of 300 sccm (70 mol% C_2H_6 and 30 mol% He). (a) Reaction rate of ethane and temperature and (b) mass fraction of dominant compounds vs. radial distance. The inset shows the zoomed-in version with the same x-axis. All data are reported on a dry basis.

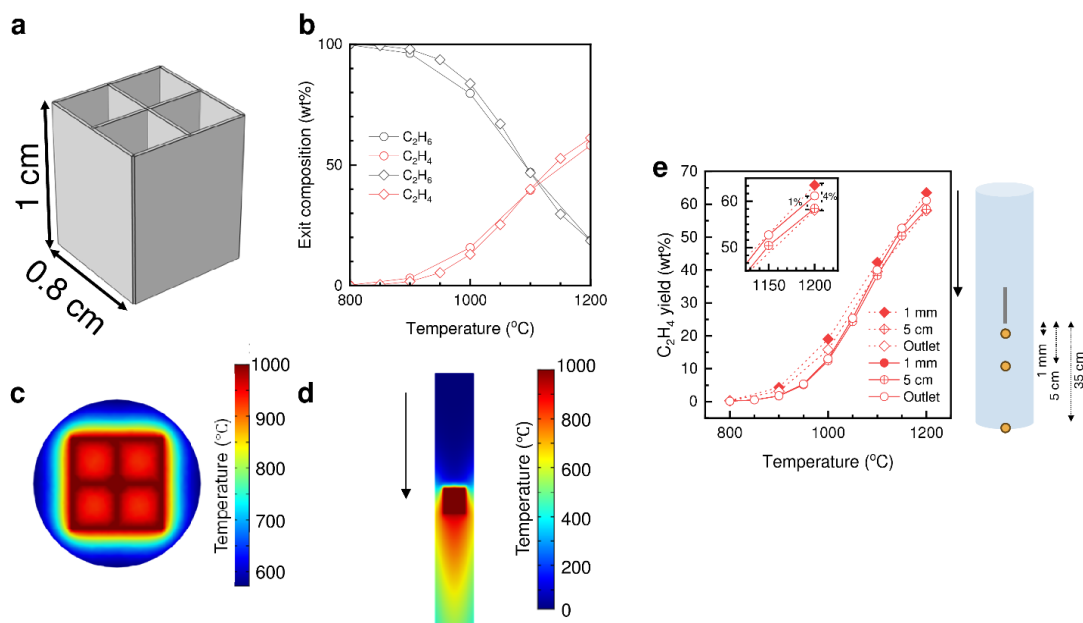


Figure C.8: Structured CFP reactor performance. (a) Schematic of the structured reactor. The thickness of each wall is 0.21 mm. (b) Exit composition in a CFP reactor of length 1 cm (circles) and a structured reactor (diamonds) with a total inlet flow rate of 500 and 83.33 sccm, respectively, with 70 mol% C_2H_6 and 30 mol% He. (c) Top and (d) front view of temperature profile in structured reactor at 1000 °C. The arrow shows the flow direction. (e) $Y_{C_2H_4}$ at various points downstream of the element in structured (dotted lines) and CFP reactors (solid lines). Inset magnifies data at 1200 °C, with numbers showing the difference in $Y_{C_2H_4}$ attained immediately after the structured element and the reactor outlet. All data are reported on a dry basis.

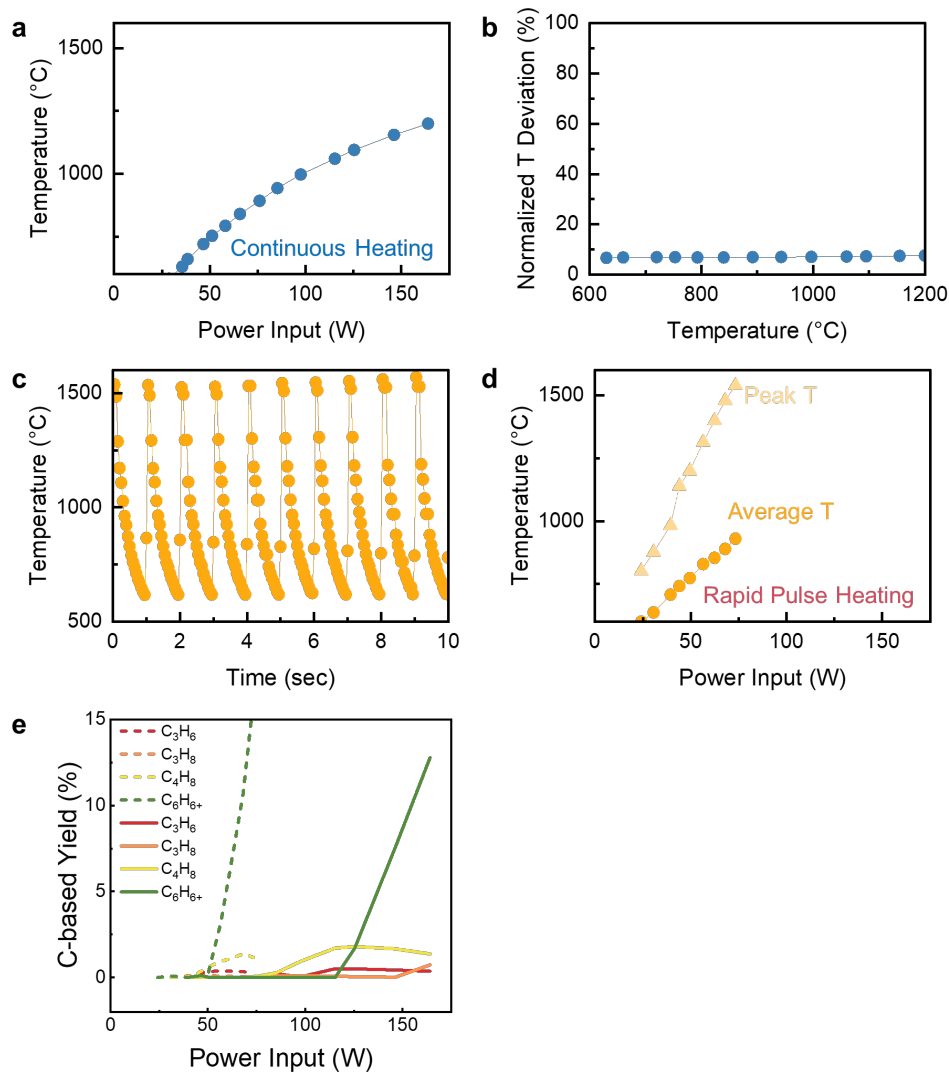


Figure C.9: Joule heating experimental data for C_2H_6 thermal cracking. (a) $38 \times 8 \times 0.21 \text{ mm}^3$ CFP temperature vs. power input in CJH. (b) Normalized temperature deviation (standard deviation of the measured area divided by the nominal CFP temperature) vs. CFP average temperature. (c) Temperature over multiple cycles at 66.7 V (5% duty for 1 s cycle), equivalent to 75 W power input under RPH. (d) Temperature-power relationship of peak (T_{peak}) and average temperatures (T_{avg}) during rapid pulse cycle. (e) C-based yields of C_3H_6 , C_3H_8 , C_4H_8 , and aromatics (C_{6+}) vs. power input of RPH (dashed lines) and CJH (continuous lines). All data are reported on a dry basis.

A power-law kinetic rate model for each product i ($i = \text{C}_2\text{H}_4, \text{C}_2\text{H}_2, \text{CH}_4, \text{C}_6\text{H}_6$) was fitted using variable partial pressure experiments. Fig. C.10 shows the fits and Table C.3 provides the rate constant a [$\text{mmol}(\text{kPa})^{-n}/\text{h}$] and reaction order n . At comparable $X_{\text{C}_2\text{H}_6}$ (45–55%), CJH shows a higher rate constant for C_2H_4 formation than RPH and approximately first-order dependence on C_2H_6 partial pressure ($n \approx 1.0$). CH_4 formation shows a higher-order dependence ($n \approx 1.22$ – 1.26), indicative of more complex reaction pathways. RPH's CH_4 fitted rate constant is ~ 5 times higher than CJH's. The C_2H_2 and aromatics formation rate constants under RPH are 19 times and 35 times higher, respectively, than CJH. C_2H_2 formation shows slightly sub-first-order kinetics ($n \approx 0.82$ – 0.84). These results suggest that at high C_2H_6 partial pressures, RPH promotes unwanted byproducts ($\text{CH}_4, \text{C}_6\text{H}_6, \text{C}_2\text{H}_2$), ultimately limiting the highest operating temperatures.

Table C.3: Kinetic parameters from power law model fitting. $r_i = a[\text{C}_2\text{H}_6]^n$, where $[\text{C}_2\text{H}_6] = \text{C}_2\text{H}_6$ partial pressure (kPa), r_i = formation rate of product i (mmol h^{-1}), a = fitted rate constant ($\text{mmol kPa}^{-n} \text{h}^{-1}$), n = reaction order. Parameters for products under CJH and RPH at comparable $X_{\text{C}_2\text{H}_6}$ with time-averaged (T_{avg}) and pulse peak (T_{peak}) temperatures. Details in Fig. C.10.

Mode	T_{avg} (°C)	T_{peak} (°C)	Fit	C_2H_4 Product	C_2H_2 Product	CH_4 Cracking	C_6H_6 Aromatics
CJH	1000	1000	a	0.58	0.03	0.02	0.00
			n	1.00	0.84	1.26	1.95
RPH	855	1540	a	0.28	0.54	0.09	0.01
			n	1.05	0.82	1.22	1.67

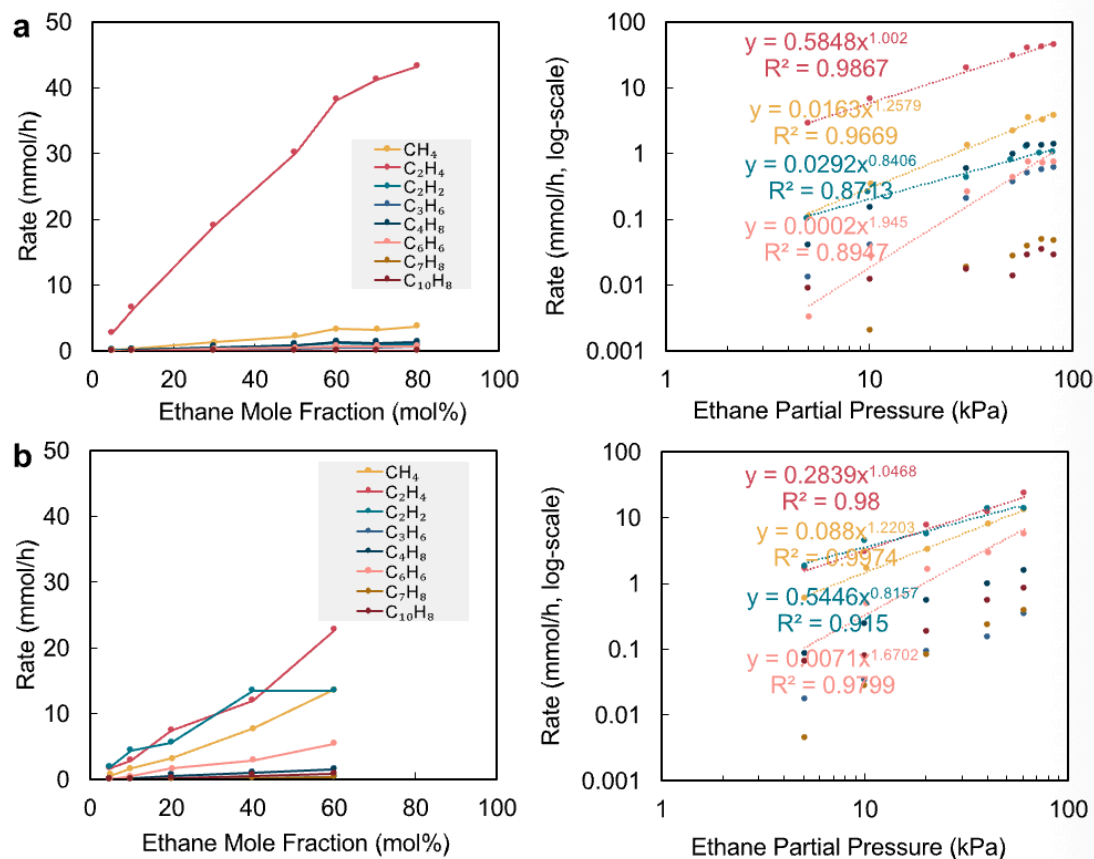


Figure C.10: Partial-pressure-dependent data in Joule reactors at comparable $X_{\text{C}_2\text{H}_6}$ (45-55%). (a) CJH reactor: 5-80 mol% C_2H_6 (5.1-81.1 kPa) at 1000 °C (5 A, 16-16.5 V, 78-82 W). The left panel shows absolute formation rates; the right panel displays power-law relationships. (b) RPH reactor: 5-60 mol% C_2H_6 (5.1-60.8 kPa) at 830 °C average/1540 °C peak (70 V, 70 W, 5% duty, 1 Hz) matched to CJH's $X_{\text{C}_2\text{H}_6}$. CFP: $38 \times 8 \times 0.21$ mm³, 1 bar, 50 sccm flow. All data are reported on a dry basis.

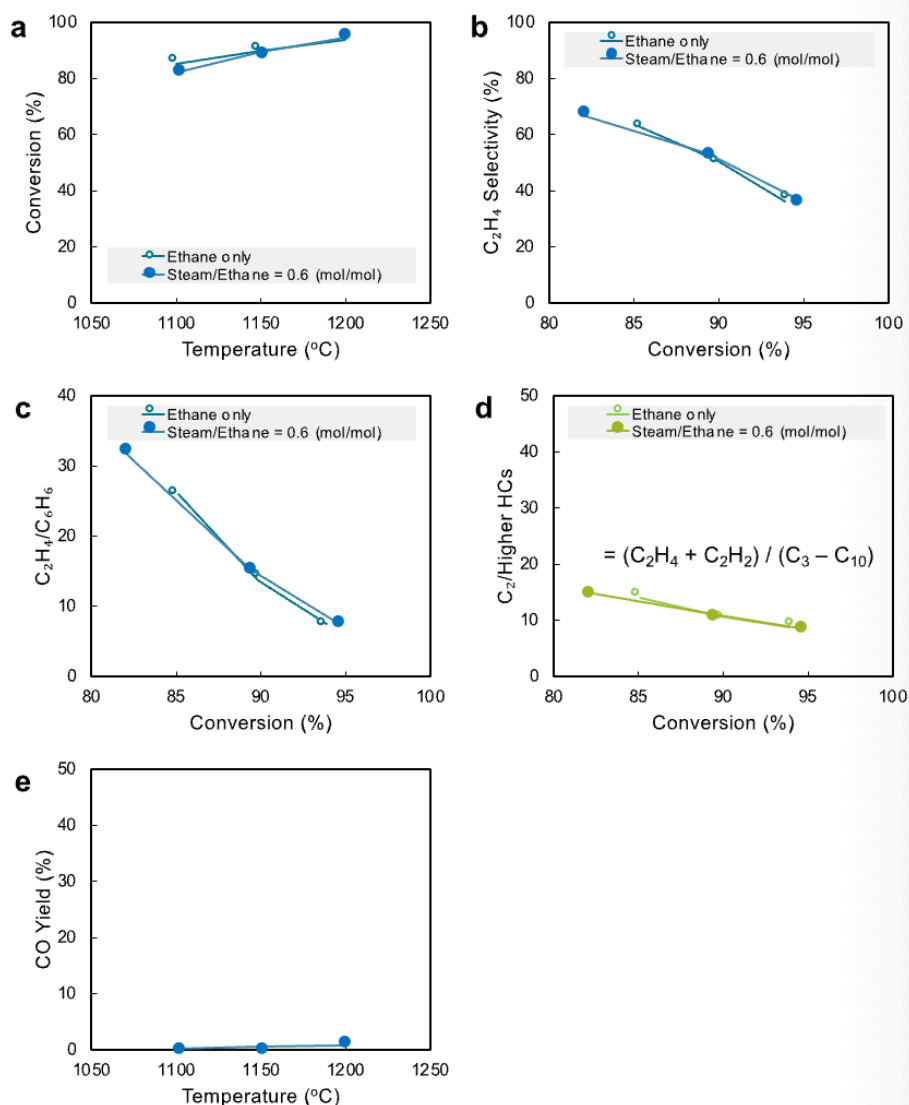


Figure C.11: H₂O effect on C₂H₆ cracking performance under CJH. Reaction conditions: flow rate = 50 sccm, 5.1 kPa of C₂H₆ and 3.04 kPa of H₂ with helium balance, H₂O/C₂H₆ = 0.6 (mol/mol) using a CFP with dimensions 38×8×0.21 mm³ at 1 bar. (a) X_{C₂H₆} vs. Temperature. (b) S_{C₂H₄} vs. X_{C₂H₆}. (c) C₂H₄/C₆H₆ ratio vs. X_{C₂H₆}. (d) Ratio of C₂H₄ + C₂H₂ over the sum of higher hydrocarbons (C₃-C₁₀) vs. X_{C₂H₆}. (e) CO yield vs. temperature. All data are reported on a dry basis.

C.2 TEA

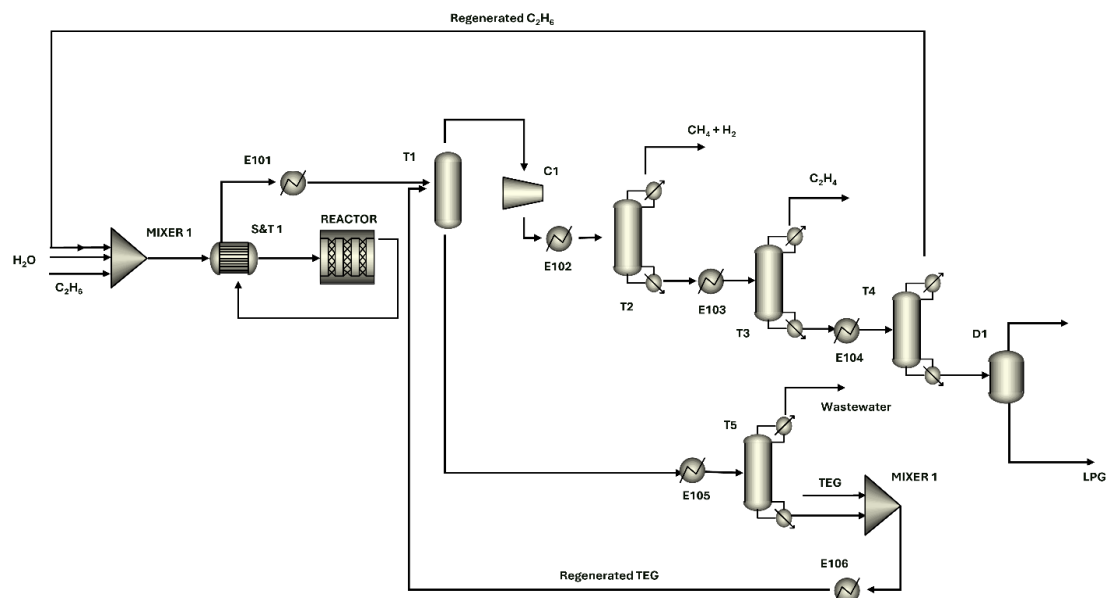


Figure C.12: A process flow diagram drawn using Aspen Plus for technoeconomic analysis. Comparison of furnace cracking (representing CH) and an ideal CJH system for noncatalytic, nonoxidative C_2H_6 thermal cracking.

C.2.1 Process Flowsheet Development

Process flowsheets for C_2H_4 production via both conventional C_2H_6 steam cracking and an ideal continuous Joule-heated (CJH) system were developed based on published reports and the MKM simulations presented in this work. The **RPlug** reactor was used to model steam cracking with a lumped kinetic scheme, while the **RStoic** reactor was used to represent the ideal and experimental CJH system (chemical

reaction equations and respective conversion mentioned in Table C.4). All units were modeled using the Peng-Rob gas model. The C_2H_4 production process consists of three main stages: (1) **Steam Cracking**: C_2H_6 and steam (3:1 vol%) are introduced into the cracking reactor (REACTOR, Fig. C.12), where they undergo steam cracking under conditions specific to each case. The hot product stream is used to preheat the feed via a heat exchanger, improving thermal efficiency. (2) **Water Removal**: The reactor effluent contains unreacted steam, which is removed in an absorption tower (T1) using triethylene glycol (TEG) at 25 °C and ambient pressure. The water-loaded TEG is regenerated in a distillation tower (T5), and the regenerated solvent is recycled back to T1. (3) **C_2H_4 Recovery**: The dehydrated stream is compressed using compressor C1 and cooled to -140 °C before entering a distillation column (T2). In T2, light byproducts (H_2 and CH_4) are separated from the C_2H_4 -rich stream. The bottom stream, containing C_2H_4 and unreacted C_2H_6 , is sent to a second column (T3), where high-purity C_2H_4 (>99.9 mol%) is recovered from the top. The remaining bottom stream is processed in a third column (T4) to recover unreacted C_2H_6 , which is then recycled to the reactor after mixing with make-up C_2H_6 stream. Process simulation in Aspen Plus V12 gives a production of $\sim 77 \text{ t h}^{-1} C_2H_4$. Table C.5 provides the key operating parameters of the main units in the C_2H_6 cracking process for all ideal cases.

Table C.4: Reactions and conversions obtained from MKM for respective cases.

Case	Reaction	$X_{C_2H_6}$
MKM- SC_{2H_4}	$C_2H_6 \rightarrow 0.88C_2H_4 + 0.07CH_4 + 0.016C_4H_8 + 0.008C_2H_2$ $+ 0.006C_3H_6 + 0.01C_6H_6 + 0.99H_2$	80.2%
MKM- XC_{2H_6}	$C_2H_6 \rightarrow 0.92C_2H_4 + 0.05CH_4 + 0.001C_4H_8 + 0.007C_2H_2$ $+ 0.006C_3H_6 + 0.004C_6H_6 + 0.01C_4H_6$ $+ 0.97H_2$	64.7%
Exp-Opt	$0.99C_2H_6 \rightarrow 0.75C_2H_4 + 0.23CH_4 + 0.01C_4H_8$ $+ 0.003C_2H_2 + 0.01C_3H_6 + 0.016C_6H_6$ $+ 1.31H_2$	80%

Table C.5: Key operating parameters of the main units in the C_2H_6 cracking processes.

Industrial steam cracking process			
Unit	T (°C)	P (bar)	Reflux ratio
Reactor	860	1	
T1	40	1	
T2	-140	30	2.715
T3	50	30	25
T4	100	25	0.5636
T5	50	0.1	1
MKM- SC_{2H_4}			
Unit	T (°C)	P (bar)	Reflux ratio
Reactor	1000	1	
T1	40	1	
T2	-140	30	3.33
T3	50	30	25
T4	100	25	0.66
T5	160	0.1	3
MKM- XC_{2H_6}			
Unit	T (°C)	P (bar)	Reflux ratio
Reactor	1000	1	
T1	40	1	

T2	-140	30	3.75
T3	50	30	24
T4	100	25	0.75
T5	40	0.1	0.1
Exp-Opt			
Unit	T (°C)	P (bar)	Reflux ratio
Reactor	1000	1	
T1	40	1	
T2	-140	30	1.95
T3	50	30	33
T4	100	25	16
T5	40	0.1	0.5

C.2.2 Assumptions used in Techno-economic Analysis

The equipment (Total Bare-Module Cost) and operating costs were estimated using the Aspen Economic Analyzer V12. Heat integration was performed using the Aspen Energy Analyzer. 10-17 heat exchangers were reported by Aspen Energy Analyzer across all cases. The key assumptions applied in the techno-economic analysis are as follows:

1. The plant capacity ($m_{C_2H_4}$) was maintained between 600,000 and 620,000 tonnes of C_2H_4 production per year.
2. The market price of C_2H_6 was assumed to be 200 USD/ton.
3. The cost of triethylene glycol (TEG) was set at 1,320 USD/ton.
4. Wastewater treatment costs were assumed to be 1.0 USD/m³.
5. The minimum selling price of C_2H_4 was calculated assuming byproduct credits for liquefied petroleum gas (LPG) and fuel gas at 550 USD/ton and 200 USD/ton, respectively.
6. The reactor design includes 144 tubes, each with a diameter of 0.12 m; tube length was calculated based on the inlet flow rate and the desired residence time.

7. To attain near ideal temperature profile for MKM, we assume CFP completely occupies the tube. Despite relatively long time on stream performance, we assume monthly replacement.
8. Labor cost was assumed to be 5,000,000 USD.
9. Maintenance cost was assumed to be 2.5 % of the total overnight cost (TOC).
10. Insurance was assumed to be 5% of TOC.
11. TOC was assumed to be 2.5 times the total bare module cost.
12. The furnace is powered using natural gas.
13. Cost of C_2H_4 (COO) is calculated using

$$COO = \frac{CAPEX + OPEX + C_{O\&M}}{m_{C_2H_4}} \quad (C.8)$$

$$CAPEX = TOC \times CCF \quad (C.9)$$

$CAPEX$ is the capital expenditure per year, $OPEX$ is the operating expenditure per year, $C_{O\&M}$ is the maintenance, insurance, and labor cost per year. CCF is the capital charge factor assumed to be 0.1 based on our economic assumptions.

14. Utility costs were taken from *Sieder et al.*[224]
15. The furnace was assumed to operate with 60% energy efficiency, whereas Joule-heated reactors were assumed to operate with 95% energy efficiency.

C.3 LCA

The life cycle assessment (LCA) conducted in this study is an attributional LCA focused solely on comparing different C_2H_4 production technologies.

Background data were sourced from the Ecoinvent 3.9 database, which provides comprehensive and region-specific inventory data. The inputs and outputs associated with the production of 1 kg of C₂H₄ for each case are summarized in Table C.6. The activities included in the life cycle impact assessment are detailed in Table C.7.

Additional assumptions include:

16. Contributions from buildings are excluded, as they may be used for other purposes and are not specific to the C₂H₄ production process.
17. Emissions were mass located between C₂H₄, LPG, and fuel gas.

Table C.6: Inputs and outputs of the 1 kg C₂H₄ production via C₂H₆ cracking.

Route	Steam cracking	MKM-SC _{2H4}	MKM-X _{C2H6}	Exp-Opt
Inputs				
C ₂ H ₆ (kg)	1.19	1.12	1.27	1.44
Water (kg)	0.59	0.52	0.75	0.83
TEG (kg)	0.002	1.6E-05	0.0001	0.0001
L.P. steam (kg)	0.0727	0.0461	0.0445	0.052
H.P. steam (kg)	3.78	2.03	10.7	2.35
L-1 refrigerant (MJ)	0.14	0.33	0.75	0.25
L-2 refrigerant (MJ)	1.61	1.55	1.43	2.1
L-5 refrigerant (MJ)	2.4	2.6	2.45	2.45
Electricity (kWh)	3.41	3.58	4.59	4.75
Fuel gas (kg)	0.59	-	-	
Outputs				
C ₂ H ₄ (kg)	1	1	1	1
Wastewater (kg)	0.62	0.66	0.44	0.88
Fuel gas (kg)	0.09	0.24	0.35	0.081
LPG (kg)	0.02	0.006	0.03	0.117
Loading Substrate				
CFP (kg)	-	9.2E-9	3E-9	6.9E-8

Table C.7: Table S7. Activities from Ecoinvent 3.9 database for life-cycle assessment of C₂H₄ production.

Product	Activities
Ethane	Ethane, [GLO], market for ethane, cut-off, S
Water	Water, tap water, [GLO], tap water production, underground water without treatment, cut-off, S
TEG	Triethylene glycol, [GLO], market for triethylene glycol, cut-off S
Steam	Steam, in chemical industry [Row], steam production, in chemical industry, cut-off S
L-1 refrigerant	Cooling energy, at -15 °C, [GLO], cooling energy production, R-134a compression refrigeration system, cut-off, S
L-2 refrigerant	Cooling energy, at -45 °C, [GLO], cooling energy production, propylene compression refrigeration system, cut-off, S
L-5 refrigerant	Cooling energy, at -100 °C, [GLO], cooling energy production, C ₃ H ₆ -C ₂ H ₄ compression refrigeration system, cut-off, S
Electricity (Natural gas)	Electricity, high voltage [US-WECC], heat and power co-generation, natural gas, combined cycle power plant, 400 Mw electrical, cut-off S
Electricity (Coal)	Electricity, high voltage [US-WECC], Electricity production, hard coal, cut-off S
Electricity (Hydropower)	Electricity, high voltage [US-WECC], Electricity production, hydro, run-of-river, cut-off S
Electricity (Solar power)	Electricity, high voltage [US-WECC], Electricity production, solar thermal parabolic trough, 50 MW, cut-off S
Electricity (Onshore wind)	Electricity, high voltage [US-WECC], Electricity production, wind, 1-3 MW turbine, onshore, cut-off S
Electricity (Offshore wind)	Electricity, high voltage [US-WECC], Electricity production, wind, 1-3 MW turbine, offshore, cut-off S
Fuel gas	Fuel gas, [GLO], market for pyrolysis fuel gas, cut-off S
Wastewater	Wastewater, average [RoW], treatment of wastewater, average, wastewater treatment, cut-off, S

C.4 Uncertainty quantification of the kinetic model

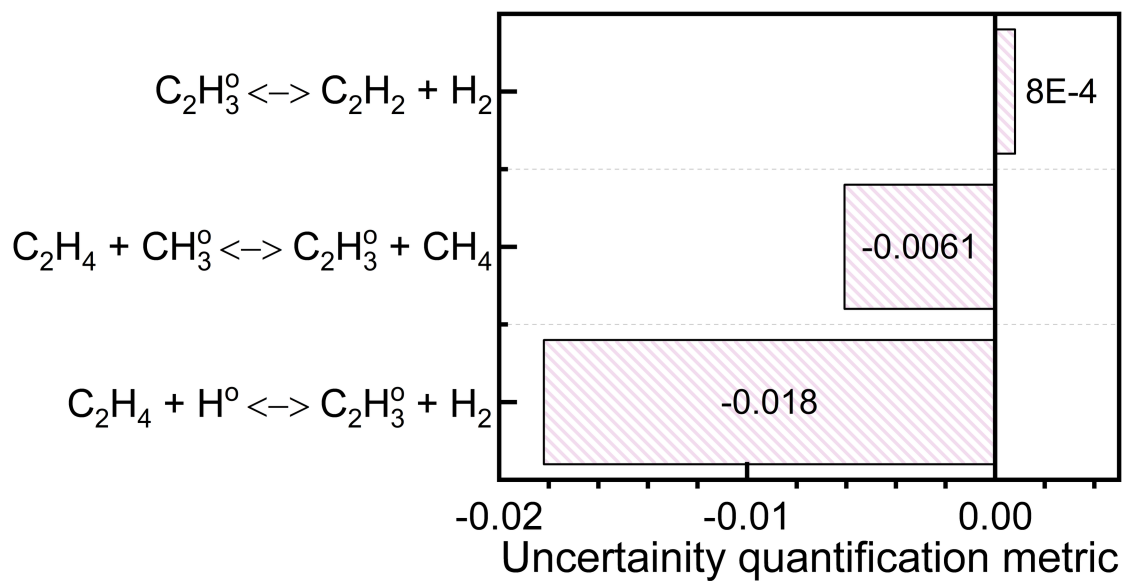


Figure C.13: Uncertainty quantification of vinyl radical-forming reactions identified by RPA in the microkinetic model at 1050 °C and residence time of 2 ms. The uncertainty quantification metric is defined as $\frac{\partial Y_{\text{C}_2\text{H}_4}}{\partial A} \times \frac{A}{Y_{\text{C}_2\text{H}_4}}$, where A is the pre-exponential component of the given reaction.

Appendix D

INSIGHTS INTO MIXING OF NON-ISOTHERMAL MULTI-POLYMER MELTS

D.1 Free surface and additional polymer mass approximation

Because the present study considers very small polymer volumes (~ 2 g), the system is highly susceptible to free-surface deformation during mixing. This behavior is governed by the Froude number (Fr), which represents the ratio of inertial to gravitational forces:

$$Fr = \frac{N^2 D^2}{g h_d} \quad (D.1)$$

where N is the revolution speed, D is the impeller diameter, g is the gravitational acceleration, and h_d is the polymer depth while at rest. For the present system ($D \sim 1$ inch and melt height ~ 0.24 inch), Fr exceeds unity even at relatively low rotational speeds, indicating that inertial forces dominate over gravity. Under these conditions, significant surface deformation and wave formation occur, making it difficult to maintain a stable, well-defined free surface in both experiments and simulations.

To ensure that the top boundary can be reasonably approximated as an open surface with constant normal stress in the computational fluid dynamics (CFD) model, additional polymer mass (Δm) was introduced to maintain a free surface at the melt

height assumed in the CFD model. The deformed surface was approximated as an axisymmetric paraboloid of the form:

$$y = h \frac{r^2}{R^2} \quad (\text{D.2})$$

where y is the height increase of the polymer-air interface, h is the maximum height increase at the reactor wall, r is the radial coordinate, and R is the vessel radius. While both rod-climbing and an increase in h were observed during operation, we only consider h , because not only is there a thin polymer film on the shaft but the polymer height on the shaft also changes with time making direct observation difficult.

Therefore, in this work extra mass was calculated using only h .

The parameter, h , was estimated from experimental observations by measuring the increase in melt height during impeller rotation relative to the static condition. For the operating conditions considered, h was found to be approximately 1 cm. Using this geometric approximation, the additional volume required to maintain a nominal flat-interface equivalent of 2 g polymer was calculated, corresponding to an additional mass of approximately 3 g of LDPE melt. This adjustment ensures that, despite surface deformation, the majority of the computational domain retains a quasi-flat free surface, allowing the use of an open boundary condition in the CFD simulations.

It is important to note that the estimated value of h was obtained at relatively low rotational speeds. As rotational speed increases, both the Froude number and the extent of surface deformation are expected to increase, leading to larger deviations from the assumed geometry. This behavior is consistent with the observed discrepancies between CFD predictions and experimental measurements at higher rotational speeds, and further supports the need for incorporating additional mass.

D.2 Material properties/55/

Table D.1: Material properties used in COMSOL simulations.

	Low-density polyethylene (LDPE)	High-density polyethylene (HDPE)
Density	750 kg/m^3	780 kg/m^3
Thermal conductivity	$0.23 \text{ W/m} \cdot \text{K}$	$0.26 \text{ W/m} \cdot \text{K}$
Heat capacity	$2260 \cdot (0.64 + 1.2 \times 10^{-3}T) \text{ J/kg} \cdot \text{K}$	$3857 \text{ J/kg} \cdot \text{K}$
Surface tension	0.0009 N/m	

D.3 PTT model fit

To determine the mobility factor (α_e), the apparent viscosity was predicted by the Giesekus formulation of the PTT model (Eq. D.3-D.5), fitted to the experimental viscosity data over the investigated shear-rate ($\dot{\gamma}$) range. The fitting results are shown in Figure D.1.

$$\eta = \mu_s + \frac{\eta_0(1-v)^2}{1 + (1 - 2\alpha_e)v} \quad (\text{D.3})$$

$$v = \frac{1 - \Lambda}{1 + (1 - 2\alpha_e)\Lambda} \quad (\text{D.4})$$

$$\Lambda^2 = \frac{1}{\frac{1}{2} + \left(\frac{1}{4} + 4\alpha_e(1 - \alpha_e)\lambda^2\dot{\gamma}^2\right)^{\frac{1}{2}}} \quad (\text{D.5})$$

Here, μ_s is solvent viscosity, η_0 is zero-shear viscosity, and λ is relaxation time.

do

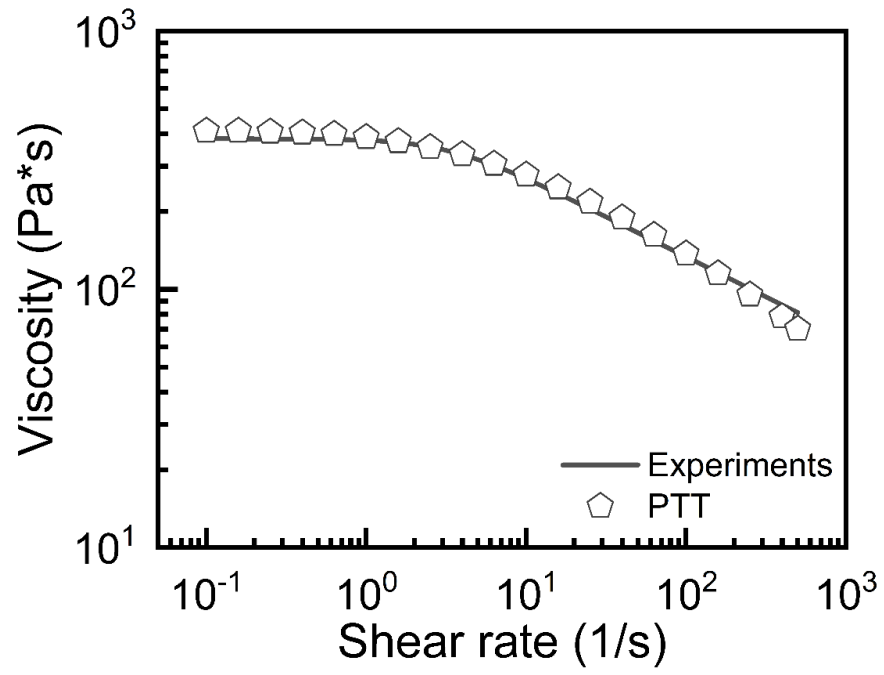


Figure D.1: Experimental viscosity data of LDPE and PTT model prediction of P_{LD} apparent viscosity at $T = 200\text{ }^{\circ}\text{C}$ ($\eta_0 = 383\text{ Pa}\cdot\text{s}$, $\lambda = \lambda_c = 0.3\text{ s}$, $\alpha_e = 0.1$, $\mu_s/\eta_0 = 0.2$, λ_c is Carreau characteristic time). [190]

D.4 PTT model prediction

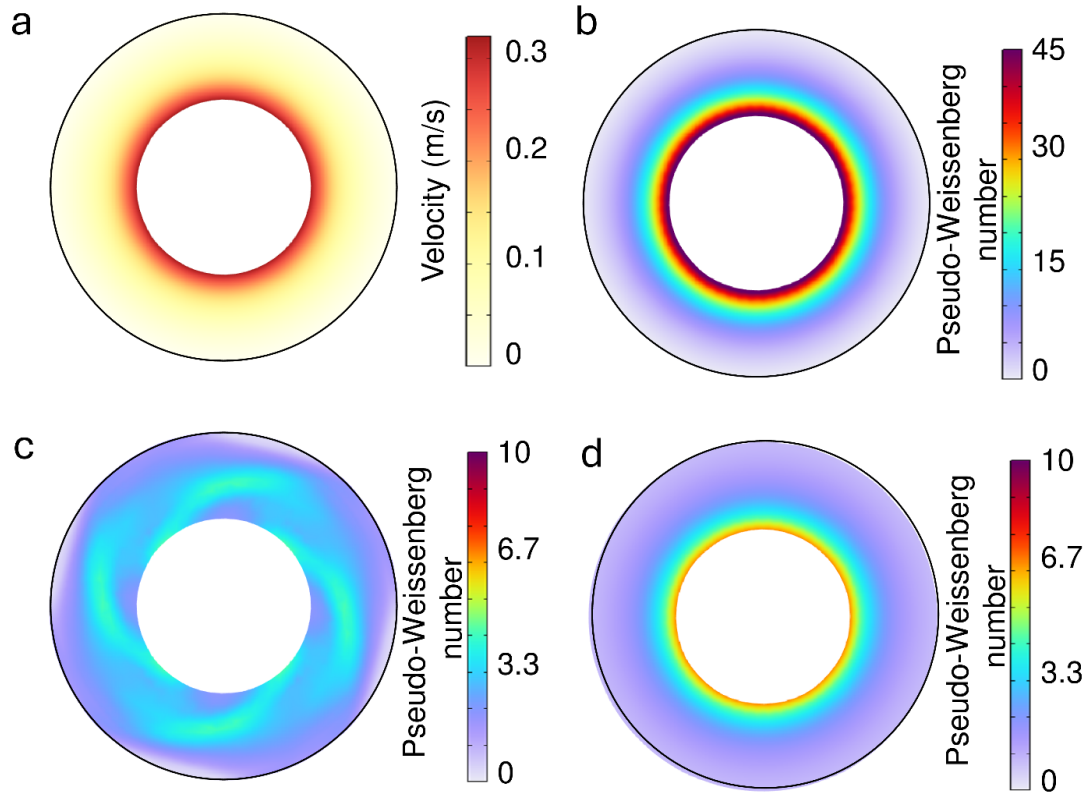


Figure D.2: P_{LD} melt mixing in a two-dimensional (2D) coaxial cylinder configuration. Top-view steady-state profiles using (a) Carreau-Yasuda model at 200 °C, (b) Carreau-Yasuda model at 200 °C, (a) PTT model at 300 °C, and (d) Carreau-Yasuda model at 300 °C.

D.5 Mixing performance and shear rate profiles for various anchor impellers

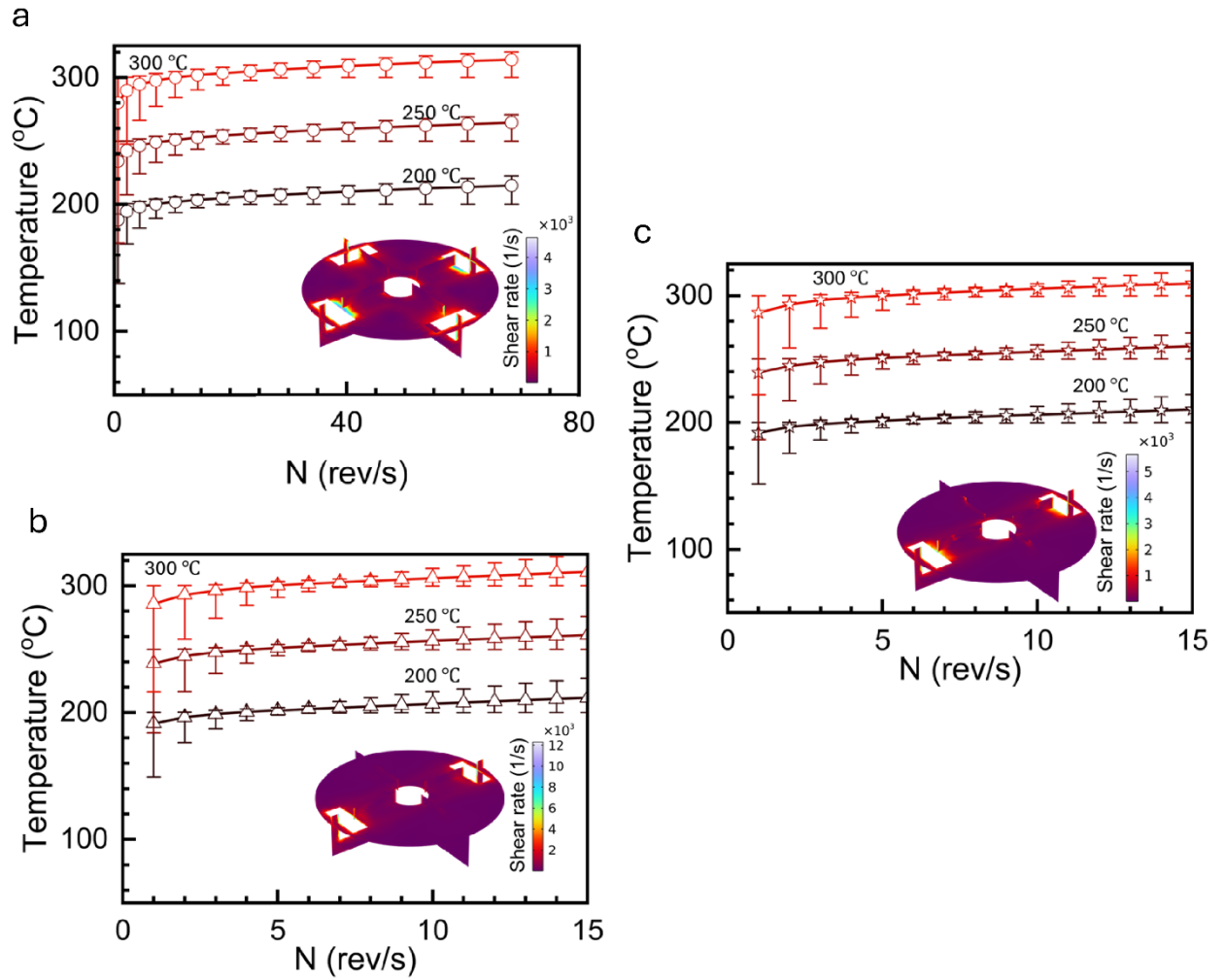


Figure D.3: Temperature vs rotation speed of three-dimensional (3D) (a) four-blade anchor impeller, (b) anchor + Flat blade turbine, and (c) anchor + pitch blade turbine. The symbols are the average temperature, and the variability bars show the minimum and maximum inside the domain. The inset shows the shear rate profile at 500 rev/min and vessel wall temperature (T_{wall}) of 300 °C.

D.6 Impact of the impeller on the temperature distribution

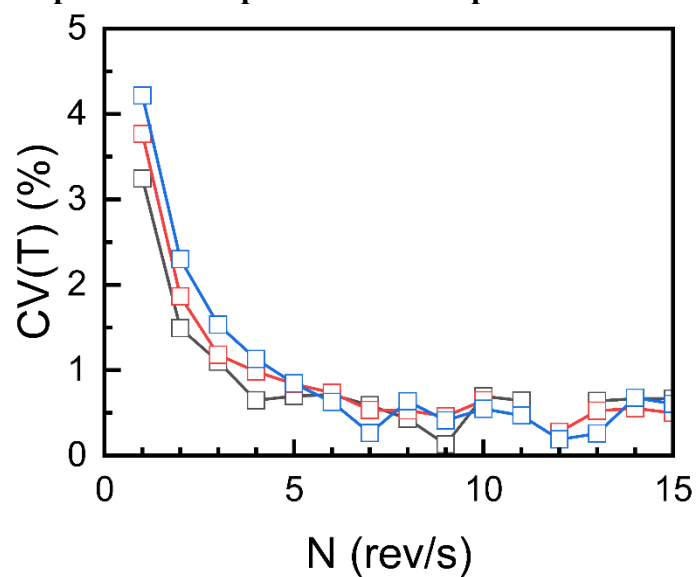


Figure D.4: Coefficient of variation of the P_{LD} melt temperature (CV(T)) using an anchor impeller with N ranging from 1 - 15 rev/s. CV(T) is the ratio of the volume-averaged temperature of the surrogate polymer to the standard deviation of the surrogate polymer temperature in the vessel.

D.7 Steady-state P_{HD} - P_{LD} interface

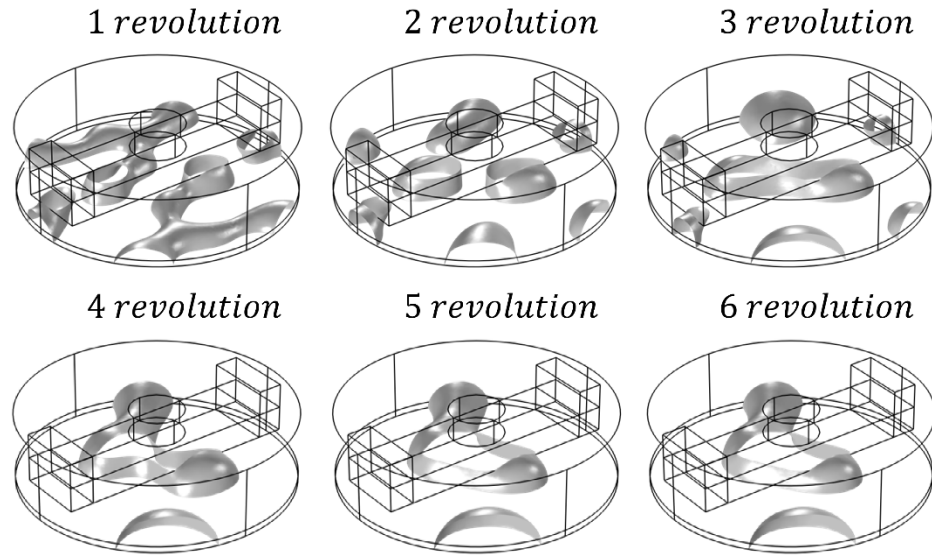


Figure D.5: P_{HD} - P_{LD} interface, represented by the silver surface, after each revolution for the anchor impeller rotating at 500 rev/min and T_{wall} of 300 °C

D.8 Schematic of the design space of polymer-polymer mixing

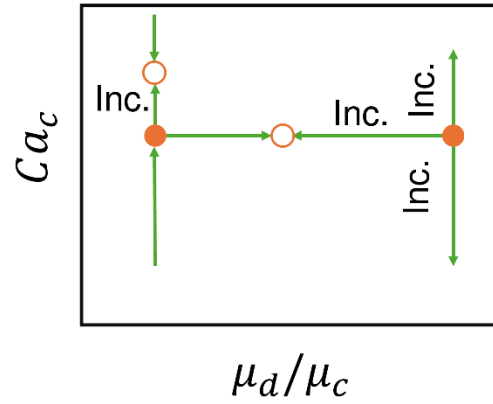


Figure D.6: Schematic of the design space illustrating factors influencing specific interfacial area. Arrows show the direction of increase (Inc.). Hollow circles designate local maxima, and filled circles designate the basis set for movement across the design space. $\frac{\mu_d}{\mu_c}$ is the ratio of the viscosity of the dispersed (μ_d) to continuous phase (μ_c), and Ca_c is the capillary number of the continuous phase.

Appendix E

INTEGRATION OF PLASTIC-DERIVED NAPHTHA IN INDUSTRIAL STEAM CRACKING VIA RETROFITTING AND MICROKINETIC-GUIDED OPTIMIZATION

E.1 TEA Assumptions

The equipment (Total Bare-Module Cost) and operating costs were estimated using the Aspen Economic Analyzer V12. Heat integration was performed using the Aspen Energy Analyzer. 10-17 heat exchangers were reported by Aspen Energy Analyzer across all cases. The key assumptions applied in the techno-economic analysis are as follows:

18. The plant capacity ($m_{C_2H_4} + m_{C_3H_6}$) was maintained between around 1.8 MT/yr.
19. The market price of naphtha was assumed to be 636 USD/ton.
20. The cost of water was assumed to be 0.2 USD/ton.
21. The cost of H₂ was assumed to be 2100 USD/ton.
22. Wastewater treatment costs were assumed to be 1.0 USD/m³.
23. The minimum selling price of olefins was calculated assuming byproduct credits for BTX and fuel gas at 1000 USD/ton and 200 USD/ton, respectively.
24. Type 3A molecular sieve was used for water removal.
25. Selective hydrogenation catalyst cost was obtained using CatCost.
26. Labor cost was assumed to be 5,000,000 USD.

27. Maintenance cost was assumed to be 2.5 % of the total overnight cost (TOC).
28. Insurance was assumed to be 5% of TOC.
29. TOC was assumed to be 2.5 times the total bare module cost.
30. The furnace is powered using natural gas.
31. Cost of olefin (COO) is calculated using

$$COO = \frac{CAPEX + OPEX + C_{O\&M}}{m_{C_2H_4} + m_{C_3H_6}} \quad (E.1)$$

$$CAPEX = TOC \times CCF \quad (E.2)$$

CAPEX is the capital expenditure per year, *OPEX* is the operating expenditure per year, *C_{O&M}* is the maintenance, insurance, and labor cost per year. *CCF* is the capital charge factor assumed to be 0.1 based on our economic assumptions.

32. Utility costs were taken from *Sieder et al.*[224]
33. The furnace was assumed to operate with 80% energy efficiency.
34. The upper limit of 25% plastic naphtha integration was found assuming complete recycling of produced plastics.

E.2 Kinetic modeling assumptions and validation

35. The microkinetic model was solved using a 0D plug-flow reactor representation implemented in OpenMKM.
36. All hydrocarbon components were represented as normal alkanes. When a specific carbon-number alkane was not available in the microkinetic mechanism, its mass fraction was assigned to the nearest lower carbon-number alkane present in the model.

37. Helium was used as a surrogate for steam in the microkinetic simulations, with the same mole-fraction dilution level applied.
38. For each temperature, the residence time was selected based on the reactor length that maximized olefin yield. This choice was consistent with the industrial data used for model validation.
39. Experimental data were obtained from the literature for validation and shown in Table E.1.[12, 62]

Table E.1: Microkinetic model validation. Naphtha composition picked from Spallina et al.[62] ($T = 850\text{ }^{\circ}\text{C}$, $\text{SDR} = 0.5\text{ kg}_{\text{steam}}/\text{kg}_{\text{naphtha}}$, all values reported in dry wt%)

	C_2H_4	C_3H_6	CH_4	C_4H_6	C_6H_6	C_4H_8	C_7H_8	C_8H_8	C_3H_8	C_2H_6
Literature	32.4	14.5	16.3	5.4	9.6	3.3	3.4	1.2	0.3	3
MKM	32.4	16	13.6	7.7	8.4	7.5	2.8	1.9	1.2	1.9

	H_2	C_8H_{10}	C_4H_{10}	C_2H_2	C_3H_4	C_5H_{12}	C_5H_{10}	C_9H_{12}	$C_{12}H_{26}$	C_9H_{20}
Literature	0.4	2.2	0.1	1.2	1.5	-	-	0.3	3.3	0.3
MKM	0.7	0.8	0.5	0.3	0.3	2.4	0.6	0.2	-	-

E.3 Benchmark Key operating parameters

Table E.2: Key operating parameters of the main units in the naphtha cracking process.

	Temperature	Pressure	Reflux ratio	Feed-to-distillate ratio	Number of stages
Demethanizer	6 $^{\circ}\text{C}$	31 bar	2.7	0.48	20
Deethanizer	77 $^{\circ}\text{C}$	26 bar	1.4	0.74	28
Depropanizer	103 $^{\circ}\text{C}$	16 bar	1.9	0.73	50
Debutanizer	124 $^{\circ}\text{C}$	3 bar	0.3	0.86	14
C2-separator	-12 $^{\circ}\text{C}$	18 bar	3.9	0.92	64
C3-separator	59 $^{\circ}\text{C}$	21 bar	16.5	0.97	254

E.4 Temperature sensitivity of plastic-derived naphtha

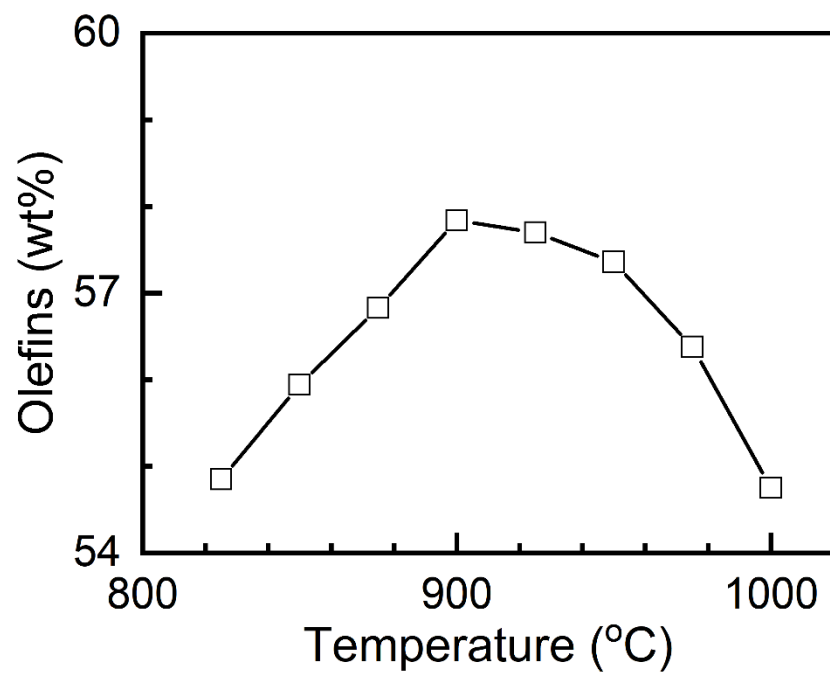


Figure E.1: Cracking temperature vs maximum olefin production, assuming the plastic-derived naphtha composition obtained from *Sun et al.*[49]

E.5 Impact of the population density of the plastic-derived naphtha production state

A modified version of the equation reported by *Hernandez et al.*, [216] was used to relate the population density to plastic collection and separating cost.

$$Cost_{USA,2026} = 0.4426 \times Pop\ density \left(\frac{inhab}{km^2} \right)^{-0.142} \times \frac{GDP_{USA}}{GDP_{Italy}} \times \frac{PI_{2026}}{PI_{2009}} \quad (E.3)$$

Here, Pop density is the population density, GDP is gross domestic product per person, and PI is the price index.

The plastic collection and sorting cost was related to plastic-derived naphtha MSP ($MSP_{PNaphtha}$), assuming a linear fit as shown in *Vance et al.* [52]

$$MSP_{PNaphtha} = 1.2 \times Cost_{USA,2026} + 260 \quad (E.4)$$

Linear fit was also done for each scenario discussed in this work to relate olefins MSP to plastic-derived naphtha MSP. Slope and constant is reported in Table E.3.

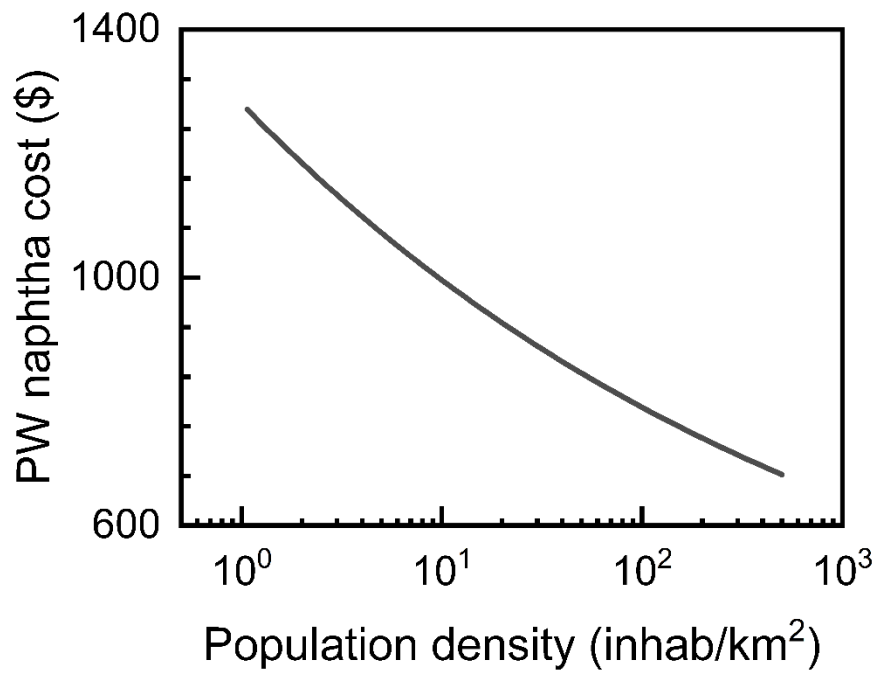


Figure E.2: PW naphtha cost vs. popouluation density.

Table E.3: Linear fit for respective scenarios.

	Slope	Constant
Scenario 1	0.12	1311.3
Scenario 2	0.56	1405.1
Scenario 3	0.11	1252
Scenario 4	0.55	977.6
Scenario 5	0.53	956.7

E.6 Optimal key operating variables

Table E.4: Key operating parameters of the main units in the optimal plastic-derived naphtha integrated cracking process.

	Temperature	Pressure	Reflux ratio	Feed-to-distillate ratio	Number of stages
Demethanizer	5 °C	31 bar	2.7	0.45	20
Deethanizer	79 °C	26 bar	1.1	0.74	28
Depropanizer	102 °C	16 bar	1.8	0.70	50
Debutanizer	124 °C	3 bar	0.3	0.89	14
C2-seperator	-12 °C	18 bar	3.4	0.93	64
C3-seperator	59 °C	21 bar	14.3	0.96	254

E.7 Impact of steam dilution ratio

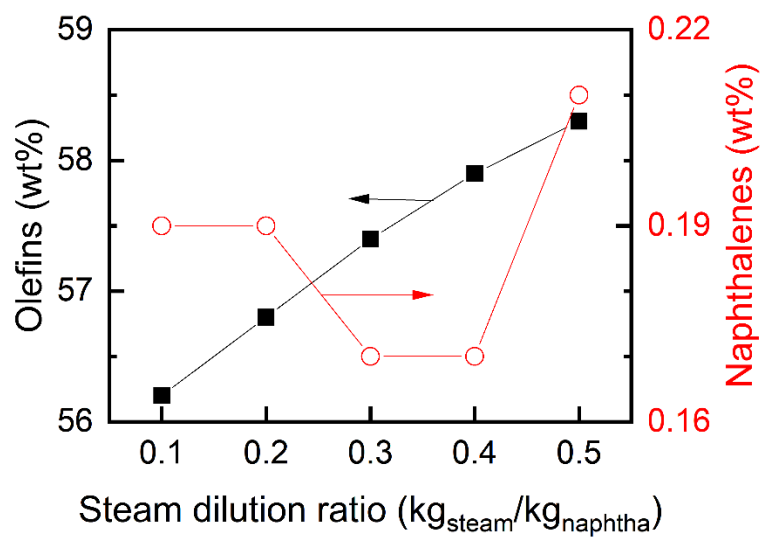


Figure E.3: Impact of steam dilution ratio on olefins and naphthalene (coke surrogate). Olefin production decreases with decreases in steam dilution, while minimal naphthalene is seen around 0.3-0.4 SDR.