

# **Transient Kinetic Modeling and Process Intensification via Rapid Pulse Joule Heating**

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The chemical industry faces mounting pressure to decarbonize; resistive (Joule) heating offers a scalable route to deliver clean process heat with millisecond-scale thermal response times that heat transfer via combustion cannot match. This makes electrically heated reactors natural candidates for forced dynamic operation. This strategy, rooted in optimal control theory, established that periodically forcing a nonlinear system away from its steady state can yield enhanced performance. Rapid pulse (Joule) heating (RPH) is a direct embodiment of this strategy. Scattered yet compelling experimental evidence for RPH performance gains has been reported, yet the mechanistic origins and design principles governing them remain unresolved. This thesis develops a transient microkinetic and process modeling framework advancing RPH along three axes: mechanistic explanation of observed enhancements, rational process intensification, and extension to novel chemistries inaccessible under steady-state operation.

Prototype reaction networks isolate the intrinsic kinetic advantage of dynamic operation, demonstrating that high-temperature excursions disproportionately accelerate rates and elevate time-averaged performance. These insights are extended to catalytic systems using transient microkinetic models, resolving experimentally observed but mechanistically opaque RPH enhancements for  $\text{NH}_3$  decomposition over  $\text{Ru}/\text{Al}_2\text{O}_3$ . Millisecond-scale temperature pulses periodically relieve  $\text{NH}_x^*$  poisoning of active Ru sites, enhancing the rate by 3-8x compared to conventional continuous operation. For the first time, we integrate temperature-dependent strain and site population to model their effect on kinetics.

Next, RPH is applied to the industrially critical steam methane reforming (SMR)–water-gas shift (WGS) process. Temperature modulation temporally accelerates the SMR at high temperatures and promotes the equilibrium-limited, low temperature WGS reaction during the colder temperatures of a pulse, intensifying the conventional three reactors (SMR and two WGS reactors) into one with high H<sub>2</sub>/CO selectivity.

Finally, RPH is extended to access reaction regimes unreachable under a single-step steady-state non-catalytic process. Co-feeding abundant CH<sub>4</sub> and CO<sub>2</sub> under pulsed heating simultaneously activates methane coupling and in situ CO<sub>2</sub> reduction. This generates a tailored syngas–C<sub>2</sub> mixture suited for downstream hydroformylation.

Translating mechanistic insights into transferable design rules requires navigating a high-dimensional space spanning kinetic, thermodynamic, and operating variables. A machine-learning workflow, combining active-learning-guided sampling with interpretable decision tree classifiers, systematically identifies the nonlinear interactions governing RPH performance and actionable insights for *a priori* prediction of conversion and selectivity gains across chemistries and catalyst–reactor combinations. Together, these findings establish RPH as a broadly applicable, transferable, intensification strategy for designing next-generation electrified chemical processes.