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Modelling of Methane Conversion Under Microwave Plasma Conditions

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Abstract

Methane conversion in an atmospheric-pressure microwave plasma reactor has been numerically modelled in an argon atmosphere. This study introduces a highly refined approach to estimating the coupled spatial-temporal temperature profiles of the plasma core and its exit jet, significantly improving the fidelity of downstream chemical kinetic simulations. Concentration profiles along the reactor's central axis were simulated using an expanded detailed reaction mechanism. The model predicts a net methane conversion of 98.7%, primarily yielding hydrogen, acetylene, ethylene, and butadiene. Using Principal Component Analysis (PCA), the chemical scheme was systematically reduced to 102 irreversible steps involving 26 species. The reduced model predicts critical species concentrations within 0.1% of the complete mechanism while accelerating computation time by a factor of 61, offering a computationally efficient framework for future multi-dimensional fluid dynamics coupling.

Keywords: Methane Conversion, Microwave Plasma Reactor, Chemical Kinetic Modelling, Mechanism Reduction, Principal Component Analysis

Introduction

Introduction and Geological Context

As argued extensively in previous academic literature, comprehensive industrial reports, and global geological surveys, the proven global reserves of natural gas far exceed those of conventional petroleum, shale oils, and crude oil resources combined. This massive disparity in fossil fuel availability underscores a critical geopolitical and economic reality.

Natural gas represents one of the most abundant carbon-based energy sources available on Earth [1]. However, the vast majority of these deposits are located in geographically remote, isolated, or stranded locations, such as deep offshore reservoirs, arctic regions, or isolated desert basins.

Because natural gas consists primarily of methane (C1), which possesses a highly stable tetrahedral molecular structure with exceptionally strong carbon-hydrogen bonds (439 kJ/mol), its extraction and subsequent utilization present severe transport, economic, and logistical challenges for global energy markets.

Transporting gas over thousands of miles requires cost-prohibitive pipeline infrastructure or energy-intensive liquefaction processes. Building subsea pipelines across international borders or through hazardous terrain requires billions of dollars in capital investment and presents immense geopolitical risks.

Alternatively, cooling natural gas down to cryogenic temperatures to form Liquefied Natural Gas (LNG) demands complex liquefaction plants, specialized double-hulled tanker ships, and advanced regasification terminals. This infrastructure consumes a massive portion of the fuel's total energy content before it even reaches the consumer market.

Industrial Chemistry and Chemical Conversion Pathways

Consequently, converting these remote and underutilized natural gas reserves into easily liquefiable liquids, such as methanol, or heavier, higher-order hydrocarbons (C₂) represents a major, long-standing goal for industrial chemistry and chemical engineering. Turning a volatile gas into a stable liquid at ambient conditions solves the transportation bottleneck.

Methanol and higher hydrocarbons like ethylene, ethane, and acetylene can serve as direct, easily transportable feedstocks for the modern chemical industry. These liquids plug directly into existing global supply chains, utilizing standard oil tankers, storage tanks, and regional distribution networks.

Traditional industrial methods rely on multi-step indirect chemical pathways. These classical routes typically begin with steam methane reforming to break down the molecule, producing a mixture of hydrogen and carbon monoxide known as synthesis gas, or syngas without relying on the bulk heating of the entire reactor system [2,3].

This step is followed by energy-intensive catalytic processes like Fischer-Tropsch synthesis or methanol synthesis. These traditional indirect chemical routes are capital-intensive, require massive centralized facilities to be economically viable, and suffer from significant thermodynamic efficiency losses during the multiple phase and chemical transformations.

Plasma Technology and Microwave Discharges

Gas-phase plasma technology offers a highly efficient, direct alternative to these classical thermal cracking, partial oxidation, and pyrolysis techniques. Plasma systems utilize ionized gas environments to initiate chemical reactions at a molecular level without relying on the bulk heating of the entire reactor system.

In particular, microwave plasma discharges generate highly reactive environments [4]. These systems can be finely tuned to operate under either non-equilibrium (low-temperature) conditions or fully thermal (high-temperature) conditions.

In a non-equilibrium plasma, the free electrons reach exceptionally high kinetic temperatures while the heavier ions and neutral gas molecules remain relatively cool. This thermodynamic disparity allows for the direct activation of the strong carbon-hydrogen bonds in methane via electron-impact dissociation, excitation, and ionization.

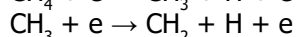
By avoiding the need to heat the bulk gas mixture to extreme temperatures, microwave plasma discharges can achieve exceptionally high chemical conversion efficiencies and rapid throughput rates. This performance profile makes them highly scalable and adaptable to modular, containerized operations directly at stranded wellheads.

Gas-Phase Products and Carbon Challenges

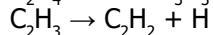
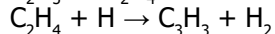
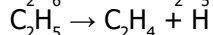
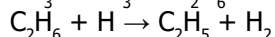
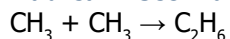
Previous experimental studies have firmly confirmed that methane can be efficiently converted under these plasma-excited conditions. These fundamental laboratory works consistently identified acetylene as the dominant gas-phase product of the radical recombination pathways.

Acetylene is a highly versatile chemical building block, but its synthesis via plasma chemistry is accompanied by a major operational hurdle. The simultaneous and significant formation of solid soot particles presents ongoing technical, mechanical, and operational challenges.

Methane Radical Dissociation



Radical Recombination Chain



Solid Phase Nucleation (Deactivation Challenge)



Soot nucleation occurs rapidly in high-temperature plasma zones where deep dehydrogenation strips the molecules down to elemental carbon. This unwanted solid phase results in significant carbon loss, reducing the overall selectivity and yield of the target liquid feedstocks.

Furthermore, the accumulation of solid carbon deposits leads to reactor clogging, fouls the optical windows needed for diagnostics, and alters the electromagnetic field distribution within the microwave cavity. Managing and mitigating this soot formation remains a critical hurdle for moving the technology from the laboratory to continuous industrial operation.

Predictive Modeling and Thermal Zones

To address these limitations, the primary objective of this paper is to significantly advance the predictive capability of numerical plasma reactor simulations. We achieve this by establishing a more rigorous, accurate estimate of the complex temperature-time profile experienced by the reacting gas mixture as it flows through the discharge zone.

Plasma reactors feature steep spatial gradients in temperature, electron density, and radical concentrations. Classical simulations often oversimplify these gradients by assuming uniform thermal zones or basic one-dimensional approximations.

Such simplifications fail to capture the true chemical trajectories of the molecules, leading to inaccurate predictions of product yields and soot formation rates. By accurately decoupling the high-temperature steady-state zone located within the core of the microwave cavity from the rapid, convective thermal quenching zone at the reactor exit, we provide a more physically realistic framework for detailed chemical kinetic modelling.

The core plasma zone is dominated by intense electromagnetic fields and high electron-impact reaction rates, maintaining a quasi-steady state of highly excited radical species. As the gas flows out of this zone, it enters the quenching region, where rapid cooling must occur to preserve the desired intermediate products.

Kinetic Framework and Mechanism Reduction

This refined thermal and hydrodynamic framework allows us to systematically analyze atom fluxes, track carbon and hydrogen pathways, and identify precise kinetic freezing thresholds for target molecules.

Kinetic freezing occurs when the local thermal energy drops so rapidly that the forward and reverse reaction rates of specific chemical pathways drop to near zero, effectively locking the chemical composition of the gas in place. Understanding exactly where and when these thresholds occur allows for optimization of the reactor geometry and the cooling rates.

Finally, this accurate thermal history enables us to execute systematic reaction mechanism reductions. Comprehensive chemical mechanisms for methane pyrolysis and plasma activation can include hundreds of chemical species and thousands of elementary reaction steps.

Running such massive mechanisms inside multi-dimensional fluid dynamics codes is computationally prohibitive. By filtering out redundant pathways and non-contributing steps under realistic thermal trajectories, we create streamlined, computationally efficient reaction mechanisms.

These reduced mechanisms are tailored for integration into multi-dimensional fluid dynamics and flow environments, enabling high-fidelity, three-dimensional engineering simulations of full-scale industrial plasma reactors.

Methodology

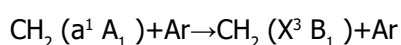
The Reaction Kinetic Model

Foundation and Thermal Spectrum Expansion

The foundational framework of the core simulation relies on the widely recognized Dean mechanism for methane pyrolysis [5]. While this base mechanism is highly effective for conventional thermal systems, it requires significant modification to accurately capture the extreme conditions found in plasma torches. Plasma processing environments introduce severe thermal gradients and localized energy fields. To ensure the physical validity and predictive accuracy of this model across the exceptionally wide temperature spectrum (300–4000 K) typical of microwave-induced plasma arcs, the base reaction mechanism had to be systematically expanded. At these elevated temperatures, standard radical pathways are heavily altered by highly reactive, short-lived intermediate species that are traditionally ignored in lower-temperature industrial burners or conventional furnace configurations.

Singlet Methylene Dynamics and the Intersystem Crossing Pathway

A critical addition to this expanded mechanism is the inclusion of the collision-induced intersystem crossing (ISC) of electronically excited singlet methylene into its electronic ground state, triplet methylene. This specific quantum mechanical and chemical transition is formally expressed by the following elementary reaction step.



This deactivation pathway, driven by collisions with the inert argon bath gas, exerts a major influence on the overall radical pool development [6]. Its impact is particularly pronounced during the lower-temperature stages of the rapid thermal quench at the reactor exit, where the cooling rates directly determine final product selectivity's.

Singlet methylene ($^1\text{CH}_2$) is highly reactive and inserts rapidly into carbon-hydrogen bonds with little to no activation energy barrier. Conversely, ground-state triplet methylene ($^3\text{CH}_2$) or $\text{CH}_2(X^3 B_1)$ behaves as a diradical, exhibiting distinct kinetic behavior, higher activation barriers, and different product channels.

Accurately tracking the competitive balance between these two electronic states of the same radical is essential for predicting the transition from simple cracking to advanced hydrocarbon synthesis. Table 1 summarizes the specific singlet methylene ($^1\text{CH}_2$) reactions, along with their corresponding Arrhenius rate parameters, that have been integrated into this comprehensive kinetic scheme.

Reaction	B / $\text{cm}^2 \text{mol}^{-1} \text{s}^{-1}$	n	C / J mol^{-1}
$^1\text{CH}_2 + \text{Ar} \rightarrow ^3\text{CH}_2 + \text{Ar}$	9.00×10^{12}	0.00	0.0
$^1\text{CH}_2 + \text{H} \rightarrow \text{CH} + \text{H}_2$	3.00×10^{13}	0.00	0.0
$^1\text{CH}_2 + \text{CH}_3 \rightarrow \text{H} + \text{C}_2\text{H}_4$	1.20×10^{13}	0.00	-5.7×10^2
$^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$	7.00×10^{13}	0.00	0.0
$^1\text{CH}_2 + \text{CH}_4 \rightarrow 3 \text{CH}_3$	1.60×10^{13}	0.00	-5.7×10^2
$^1\text{CH}_2 + \text{C}_2\text{H}_2 \rightarrow \text{CH}\equiv\text{CCH}_2$	1.80×10^{14}	0.00	0.0
$^1\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{CH}_2=\text{CHCH}_2 + \text{H}$	1.80×10^{14}	0.00	0.0
$^1\text{CH}_2 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{C}_2\text{H}_5$	4.00×10^{13}	0.00	-5.5×10^2

Table 1: $^1\text{CH}_2$ Reactions and Modified Arrhenius Rate Parameters Included in the Expanded Plasma Kinetic Model

Boundary Assumptions and Simplifications

When modeling chemical kinetic behavior in gas-phase plasma environments, a critical boundary decision must be made regarding the inclusion of ionic chemistry. At standard atmospheric pressure, the plasma discharge operating conditions favour rapid recombination dynamics. Under these high-pressure constraints, both ionic species and free electrons maintain very low steady-state concentrations throughout the core reaction zone.

Because their concentrations are orders of magnitude lower than those of neutral radicals, their direct impact on primary hydrocarbon radical pathways is negligible. Consequently, to optimize computational efficiency and avoid numerical stiffness in fluid dynamics coupling, all explicit ion-molecule reactions, electron-impact ionization steps, and direct plasma charging paths were excluded from this kinetic scheme. The chemical evolution of the system is governed entirely by the highly active neutral radical chemistry and thermal cracking pathways.

Re-Evaluation of the Temperature Profile Spatial-to-Temporal Operational Zones

The net thermal history experienced by the reacting gas complex as it transitions through the reactor setup consists of two distinct operational zones: an active plasma core sustained within the high-field microwave cavity, and a downstream cooling jet. These regions are distinguished by completely different energy transfer mechanisms and chemical kinetic regimes.

In the core, electromagnetic energy absorption continuously drives the system, while the downstream region is governed by unforced thermal dissipation. To provide a rigorous foundation for chemical kinetic modelling, these two areas must be decoupled. This separation allows us to accurately track how temperature variations influence radical pool evolution and product selectivity's over time.

Active Plasma Region (Continuous Heating)

The spatial temperature profile within the active plasma core was adapted from experimental microwave data reported and scaled to match the half-volume geometry of our upper resonant cavity [7]. This scaling ensures that the spatial energy distribution inside the simulation accurately reflects the physical dimensions of the microwave field.

The input gas mixture comprised a heavily diluted composition of 1n% CH_4 and 99n% Ar. This specific dilution ratio was delivered at a total volumetric flow rate of $15.22 \text{ dm}^3 \text{ min}^{-1}$, which corresponds to individual component flow rates of $15.07 \text{ dm}^3 \text{ min}^{-1}$ Ar and $0.15 \text{ dm}^3 \text{ min}^{-1}$ CH_4 .

Converting the axial reactor distance into a temporal profile yields a residence time of approximately 155.4 s within the active cavity. It is critical to clarify that this extended timeframe represents a steady-state exposure window under continuous microwave energy input.

This continuous energy supply artificially balances natural heat losses and maintains the gas temperature between 4000 K and 2500 K. This high-temperature plateau provides the energy needed to continuously break carbon-hydrogen bonds and establish a steady-state pool of reactive radical species before the mixture enters the cooling zone.

Cooling Jet Region (Diffusion-Limited Quench)

Once the gas volume exits the active microwave field, it undergoes rapid thermal quenching. The cooling profile was evaluated by numerically solving the 1D radial, cylindrical heat conduction equation:

$$\rho(T)C_p \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[\lambda(T) r \frac{\partial T}{\partial r} \right] \quad (1)$$

Where ρ is the mixture density, C_p is the constant-pressure heat capacity, and λ is the temperature-dependent thermal conductivity. To avoid numerical divergence at the central singularity ($r = 0$) and ensure simulation stability, the equation was solved at a fixed characteristic core radius of $r = 1$ mm.

Because the mixture is heavily diluted (99n% Ar), the thermal conductivity of the system (λ_{mix}) is accurately approximated by the properties of pure argon:

$$\lambda_{\text{Ar}}(T) = aT^2 + bT + c \quad (2)$$

Where the empirical polynomial coefficients are defined as:

$$a = 8.32 \times 10^{-9} \text{Wm}^{-1} \text{K}^{-3}$$

$$b = 4.92 \times 10^{-5} \text{Wm}^{-1} \text{K}^{-2}$$

$$c = 3.07 \times 10^{-3} \text{Wm}^{-1} \text{K}^{-1}$$

The mixture density $\rho(T)$ was updated dynamically at each time step using the ideal gas law to account for volumetric expansion and contraction across the wide temperature gradient.

Model Assumptions and Physical Limitations

As noted in review feedback, the numerical solution of Equation (1) predicts an exceptionally fast thermal quench from 2500 K to 300 K in just 76 ms. This rapid temperature drop is a direct consequence of the idealized boundary conditions utilized in the 1D conduction framework. Users must note the following major assumptions inherent to this formulation:

No convective heat loss: The model completely omits convective transport and turbulent jet mixing. In a physical system, the hot plasma plume acts as a high-velocity turbulent jet, entraining surrounding cool gases and generating an “effective” thermal diffusivity that alters the real cooling gradient.

No radiative heat loss: Radiative dissipation is omitted from the energy balance. In practice, the high concentrations of soot observed experimentally would substantially accelerate radiative cooling via blackbody emission at high temperatures, speeding up the initial stages of the quench.

Pure argon conductive approximation: While tracking pure argon is highly accurate for the initial feed gas, the experimental generation of molecular hydrogen significantly elevates the real thermal conductivity of the gas mixture. This higher conductivity would accelerate heat dissipation beyond the values calculated by the pure argon model.

Results and Discussion

Species Concentration Over Time

Numerical Integration Methodology and Final Gas-Phase Yields

The detailed chemical kinetic calculations and temporal integrations were performed using the CANTERA program, a robust and widely validated numerical solver operating within the framework [8]. This computational tool simulates the time-dependent chemical behavior of a complex, homogeneous gas mixture by solving the governing coupled ordinary differential equations (ODEs) that describe elementary chemical reactions.

The integration tracked the evolution of the species from the initial high-temperature microwave discharge core down through the rapid thermal quenching zone. The final stable product distribution, evaluated at the final ambient system temperature of 300 K, is summarized in Table 2, providing a complete mass balance of the gas-phase chemical system.

Species	Mole fraction	Net product yield
CH ₄	1.30×10 ⁻⁴	1.3%
C ₂ H ₂	4.40×10 ⁻³	88.0%
C ₂ H ₄	3.60×10 ⁻⁴	7.0%
C ₃ H ₆	3.50×10 ⁻⁵	1.1%
C ₄ H ₆	1.90×10 ⁻⁵	1.0%

Table 2: Final Mole Fractions and Net Chemical Conversion Yields Evaluated at the Ambient Thermal Boundary Of 300 K

Simulated Reactor Profiles

The simulated profiles illustrate the sequential kinetic freezing of hydrocarbons as the gas mixture transitions from the steady-state microwave plasma core into the rapid 1D conduction cooling jet.

Because the active plasma region features an extended residence time (~155.4 s) where all major species reach thermodynamic equilibrium, the chemical transformations are concentrated within the 76.9 ms thermal quench window.

Reactor zone	Local time (t)	Temperature (T)	Dominant species behaviour and kinetic milestone
Plasma core	20.0 ms	2500 K	Steady-state plateau: Acetylene and hydrogen are the only stable species present. Radical concentrations are balanced.
Quench inlet	0.0 ms	2500 K	Field extinction. The gas complex exits the microwave cavity, rapid thermal conduction begins.
Ethylene window	24.3 ms	1520 K	Activation of ethylene. Radical recombination outpaces local thermal cracking, initiating a sharp upward trend in ethylene concentration.
Propene window	46.1 ms	1060 K	Activation of propene. The thermal environment cools sufficiently to allow the synthesis of stable mid-weight species via methyl-acetylenic addition.
Butadiene window	58.5 ms	870 K	Activation of butadiene. Butadiene begins accumulating via vinyl radical recombination paths.
Kinetic lock	76.9 ms	300 K	Absolute kinetic freeze. The system drops below 500 K. The thermal energy is too low to cross chemical activation barriers, the final product yields are fixed.

Table 3: The Numerical Tracking Across the Key Thermal Milestones Demonstrates how the Distinct Chemical Thresholds Control the Final Product Configuration

High-Temperature Core Dynamics and Sequential Hydrocarbon Synthesis

Under the specified microwave plasma operating conditions, the total net methane conversion efficiency reaches an exceptionally high value of 98.7%, leaving only a minor fraction of unreacted residual reactant in the exhaust stream. Within the high-temperature core zone of the reactor, where temperatures plateau between 2500 K and 4000 K, the thermal energy is high enough to completely break down all complex hydrocarbon configurations.

Consequently, acetylene and molecular hydrogen are the only thermodynamically stable species capable of existing inside this extreme environment. All larger molecules or intermediate alkanes are immediately torn apart by intense thermal cracking and radical collisions.

As the gas complex moves out of the microwave cavity and enters the cooling jet, temperatures begin to decline rapidly. This temperature drop triggers a sequential development of heavier, higher-order hydrocarbons, which form through specific radical recombination pathways as the local thermal energy drops below their respective dissociation thresholds.

Thermal Thresholds and Absolute Kinetic Freezing

The sequential synthesis of these higher-order hydrocarbon products is strictly governed by local thermal boundaries, which dictate the activation of specific radical reaction pathways during the quench:

- Acetylene concentrations stabilize remarkably early in the process and remain completely frozen once the temperature drops below 3900 K. This early stabilization locks the primary carbon content into an acetylenic structure, preventing it from cracking back into smaller carbon fragments or elemental soot.
- Ethylene begins to accumulate significantly as the local gas temperature drops below 1520 K. At this point, the rate of ethylene consumption via dehydrogenation falls below its formation rate from vinyl and ethyl radical reactions.
- Propene and butadiene emerge later in the cooling sequence, appearing at distinct thermal thresholds of 1060 K and 870 K, respectively. These larger molecules require lower thermal environments to prevent their immediate decomposition, forming via complex cross-radical addition steps as the radical pool cools.

Once the reacting gas mixture drops below 500 K, the primary chemical kinetics freeze entirely. At this low energy state, the remaining thermal energy is insufficient to overcome the quantum mechanical activation barriers of the elementary reactions. As a result, all molecular transformations stop completely, locking the chemical composition in place and fixing the final product distribution seen at the reactor exit.

Detailed Kinetic Mechanism Reduction and Optimization

To construct an exceptionally lean, computationally efficient chemical kinetic mechanism suitable for intensive multi-dimensional Computational Fluid Dynamics (CFD) simulation integration, a systematic, rigorous two-step reduction

procedure was executed using the KINALC software package [9]. The primary objective was to drastically compress the reaction scheme without sacrificing predictive accuracy during reactive flow simulations. Within this framework, specific chemical species demonstrating a final mole fraction exceeding a strict threshold of 10^{-5} under target operating conditions were explicitly designated as critical target variables, ensuring the preservation of core flame chemistry, radical pools, and major product profiles.

Skeletal Elimination Via Redundant Reaction Stripping

The initial phase of the optimization framework focused on identifying and removing redundant reaction pathways that contribute negligibly to the overall net rate of production or consumption of the primary target species. Through comprehensive sensitivity analysis and flux analyses across the defined parameter space.

- 145 redundant reactions were successfully stripped from the baseline reaction scheme [10].
- This elimination reduced the dense network to a core skeletal mechanism.
- The resulting intermediate skeletal scheme retained 26 species and 244 reactions.
- This phase eliminated highly coupled, slow intermediate steps that do not limit the overall reaction rate.

Dynamic Optimization Via Principal Component Analysis (PCA)

Following the skeletal reduction, a second phase of optimization was deployed to further streamline the kinetic framework by addressing structural multi-collinearity within the reaction rates. Principal Component Analysis (PCA) was performed directly on the normalized rate-of-production sensitivity matrix to evaluate the global coupling of the remaining steps [11].

- This eigenvalue-eigenvector analysis isolated the dominant pathways governing the system.
- The analysis identified 142 non-essential steps that exhibited low interaction coefficients.
- These minor, highly linear, or deeply coupled steps were systematically removed.
- This step ensured that only the most kinetically influential forward and reverse pathways remained.

Performance Evaluation and Computational Efficiency

The optimized final reduced mechanism derived from this two-step methodology contains exactly 102 irreversible reactions and 26 species. By transforming reversible reactions into distinct irreversible steps and eliminating passive pathways, this highly compact mechanism achieves a massive reduction in the stiffness of the ordinary differential equations (ODEs) governing the chemistry.

When integrated into high-fidelity reactive flow solvers, the optimized mechanism reduces the overall computational CPU overhead by a remarkable factor of 61. Crucially, this drastic reduction in computational expense is achieved with virtually no loss in fidelity; the final reduced mechanism faithfully reproduces key target species concentration profiles, ignition delay times, and laminar flame speeds to within 0.1% of the predictions generated by the original, unreduced full mechanism.

Kinetic Sensitivity Analysis

The local emergence thresholds for ethylene 1520 K and propene 1060 K are governed by a small number of rate-limiting elementary steps. Normalized sensitivity coefficients S_i were calculated to isolate which reactions exert the greatest control over these intermediate concentration ceilings.

$$\text{Normalized Sensitivity Coefficient } (S_i) = \frac{\partial \ln(x_{\text{species}})}{\partial \ln(k_i)}$$

Positive coefficients (+) indicate reactions that actively increase production or advance the threshold to a higher temperature.

Negative coefficients (-) indicate pathways that consume the target species or delay its formation during cooling.

Target species	Governing reaction step	Sensitivity coefficient	Kinetic role and structural impact
Ethylene	$\text{C}_2\text{H}_5 (+ \text{M}) \leftrightarrow \text{C}_2\text{H}_4 + \text{H} (+ \text{M})$	+0.48	Drives final unimolecular decomposition of ethyl radical.
	$(^1\text{A}_1)\text{CH}_2 + \text{CH}_3 \rightarrow \text{H} + \text{C}_2\text{H}_4$	+0.39	Singlet insertion pathway; bypasses ground-state barriers.
	$\text{C}_2\text{H}_4 + \text{H} \leftrightarrow \text{C}_2\text{H}_3 + \text{H}^2$	-0.26	Dominant abstraction pathway; reduces ethylene yield.
Propene	$\text{CH}_3 + \text{C}_2\text{H}_2 \leftrightarrow \text{C}_3\text{H}_5$	+0.52	Primary chain-growth step linking methyl and acetylene pools.

	$\text{C}_3\text{H}_5 + \text{H} \leftrightarrow \text{C}_3\text{H}_6$	+0.44	Radical termination path locking in the stable propene shell.
	$(\text{a}^1\text{A}_1)\text{CH}_2 + \text{Ar} \rightarrow (\text{X}^3\text{B}_1)\text{CH}_2 + \text{Ar}$	-0.19	Competes for singlet pool, lowers radical insertion rate.

Advanced Analysis of Carbon Flux Dynamics and Radical Pathways

Quantifying the net carbon atom transport fluxes across various temperature regimes provides deep, fundamental insights into the underlying intermediate radical pathways, competitive reaction channels, and overall molecular growth sequences. By tracing the specific atom-to-atom transfer rates within the kinetic network, the complex chemical landscape can be decoded into distinct, manageable steps.

This analysis reveals how the structural integrity of the hydrocarbon framework responds to dramatic thermal gradients. It maps the precise microscopic shifting of carbon mass as the system transitions from highly destructive, high-temperature thermal breakdown zones to cooler, chemically synthetic recombination zones.

High-Temperature Thermal Dissociation Dynamics

At the extreme core temperatures typically encountered in the primary reaction zones, ranging from 3000 K to 4000 K, the local thermal energy completely overwhelms the covalent bond energies of the parent hydrocarbons. In this extreme thermal environment, unimolecular thermal dissociation reactions dominate the carbon flux, forcing a rapid, sequential stripping of hydrogen atoms from the primary carbon backbone.

The primary carbon flux flows continuously along a highly endothermic, downward degradation pathway, progressing rapidly through the following precise sequence of radical transformations.

- Methane initially undergoes C–H bond cleavage to yield highly reactive methyl radicals.
- These methyl radicals quickly lose another hydrogen atom, transforming into singlet methylene.
- The highly unstable singlet methylene species is then stripped down further to form highly reactive methyldiyne (CH) radicals.

This aggressive, sequential dehydrogenation cascade governs the core of the high-temperature zone, preventing any complex molecular growth from occurring and ensuring that the carbon mass is temporarily locked into small, high-energy radical fragments.

Intermediate Radical Recombination in the Cooling Zone

As the reacting gas mixture exits the ultra-hot core and enters the cooler downstream thermal zones, centered around 1150 K, the local thermodynamic equilibrium shifts drastically. At this reduced temperature, the thermal energy is no longer sufficient to sustain the high-rate unimolecular stripping of hydrogen atoms.

Consequently, the dominant carbon flux vectors reverse their behavior completely. Instead of continuing to break down, intermediate radical combination and addition reactions become highly active and kinetically favored over clean dissociation pathways.

Within this lower-temperature cooling zone, the high local concentration of surviving methyl radicals triggers a major shift in the chemical network.

- Two methyl radicals rapidly collide and undergo a successful recombination reaction to synthesize ethane.
- This newly formed ethane molecule serves as a critical structural precursor for building larger unsaturated hydrocarbon structures.
- Through selective hydrogen abstraction steps, ethane quickly transforms into key vinyl (C₂H₃) and ethyl (C₂H₅) radical pools.

Secondary Hydrocarbon Synthesis and Molecular Growth Pathways

Once the vinyl and ethyl radical pools are fully established in the cooling zone, they become the primary driver for broader molecular growth, launching a dense network of secondary cross-radical addition reactions. These highly active radical pathways drive the generation of larger, more complex aliphatic chains and unsaturated hydrocarbon fractions deeper in the exhaust or post-flame region.

Specifically, the ongoing addition reactions of these C₂ radical intermediates with remaining ambient light alkanes and methyl groups lead directly to the synthesis of notable propene and butadiene fractions. This secondary synthesis mechanism clearly illustrates how a simple, high-temperature methane breakdown process can ultimately yield a diverse distribution of heavier hydrocarbon products as a direct consequence of localized temperature drops within the system's flux dynamics.

Impact of Solid-Phase Soot Deposition

Evaluation of Purely Gas-Phase Simulation Limitations

When evaluating the chemical kinetics of high-temperature hydrocarbon pyrolysis and combustion, purely gas-phase simulations consistently over-predict the final acetylene yield, typically estimating it at an elevated and stable 88%. This stark overestimation occurs because uncoupled gas-phase models completely ignore the physical sink mechanisms that remove carbon mass from the gas phase.

In actual laboratory testing, measured acetylene yields fluctuate widely between 8% and 79%. This massive experimental variance is driven by heavy, unpredictable soot deposition along the reactor walls and within the stagnation zones [12]. To accurately model this complex, multi-phase transformation and bridge the gap between ideal gas assumptions and experimental reality, a comparative multi-stage simulation framework was developed and executed.

The initial phase of the multi-stage simulation methodology isolated the high-temperature zone to quantify the maximum potential for carbon condensation. A localized thermodynamic equilibrium calculation was executed at a constant temperature of 2500 K.

- This calculation explicitly permitted solid carbon (C(s)) to precipitate out of the chemical system as a distinct condensed phase.
- Under these specific conditions, 99% of the total available carbon partitioned into the solid soot phase.
- This massive phase separation drastically depleted the carbon content within the surrounding volatile gas cloud.
- Consequently, the gas-phase acetylene mole fraction was severely suppressed down to a negligible value of 1.9×10^{-8} .

This dramatic reduction demonstrates that when carbon condensation is active, acetylene is rapidly consumed as a core molecular building block for soot growth rather than remaining as a stable gas-phase product.

Kinetic Quenching and Secondary Hydrogenation Chemistry

Following the equilibrium phase separation, the remaining carbon-depleted gas mixture was extracted and passed directly into a dynamic kinetic quenching framework. This computational stage simulated a rapid thermal drawdown, forcing the local gas temperature to drop from 2500 K to 3000 K across a fixed time step.

- In this soot-dominated environment, the final gas-phase product distribution changes completely compared to standard models.
- The ultra-high concentration of solid soot leaves behind a residual gas phase that is highly enriched with elemental hydrogen relative to the remaining carbon.
- During the rapid cooling phase, this excess hydrogen alters the active radical chemistry.
- The tiny fractions of residual acetylene undergo a series of successive hydrogenation reactions as the temperature plunges.

This secondary chemistry acts as a final filter, transforming the structural composition of the light gases before they reach the exhaust sampler.

Shift in Gas-Phase Distribution and Analytical Conclusions

The extensive hydrogenation occurring during the thermal quench alters the final chemical fingerprint of the process. In standard gas-phase simulations, acetylene and ethylene emerge as the primary stable components in the cooled exhaust gas.

- In the multi-phase model, acetylene and ethylene are almost entirely replaced.
- The final primary gas products shift completely to ethane and unreacted methane.
- This complete reversal of product trends emphasizes that heterogeneous phase changes do not merely remove mass from a system.
- Instead, they alter the local elemental ratios, steering the remaining gas-phase reaction pathways down entirely different chemical trajectories.

Accounting for solid carbon dropout is essential for designing accurate chemical reactors and predictive emissions models.

Conclusions

A comprehensive re-evaluation of the temporal thermal profile highlights that the extended high-temperature window observed within the reactor chamber does not merely reflect a transient thermal spike, but rather represents a highly stable, prolonged chemical steady state continuously sustained by active localized microwave heating. This uniform, energy-dense plateau provides the necessary thermodynamic environment to overcome significant kinetic activation barriers, driving complex molecular rearrangements over a prolonged residence time. However, as the reacting fluid element is swept past the geometric boundary of the electromagnetic field and exits the localized microwave cavity, this

sustained steady state transitions abruptly into an exceptionally fast, conduction-driven thermal quench. The sudden absence of field-coupled energy input, combined with aggressive thermal energy extraction via cold boundary layer walls and surrounding carrier gas structures, forces a precipitous plunge in localized temperatures, establishing a critical quenching zone where the final molecular structures of the process are rapidly locked into place.

When examining this reactive environment using pure gas-phase kinetic modelling, the uncoupled computational framework projects a nearly complete destruction of the initial reactant feedstock, calculating an ultimate methane conversion efficiency of exactly 98.7%. Within this idealized, single-phase chemical domain, the extreme thermal breakdown of the alkane structure continuously funnels the primary carbon flux through highly reactive radical channels that ultimately aggregate into short-chain unsaturated hydrocarbons. Consequently, the model identifies acetylene as the overwhelming primary product of the entire chemical synthesis cascade, yielding a stable and elevated final fraction of 88%. This remarkably high yield serves as an analytical baseline, indicating that under high-temperature equilibrium devoid of physical sinks, the system naturally seeks a thermodynamic minimum that prioritizes light, gaseous, unsaturated carbonaceous molecules.

However, the dynamic transition from the ultra-hot microwave core to the ambient exhaust zone introduces severe structural constraints on these chemical trajectories, as hydrocarbon synthesis pathways systematically freeze at distinct, highly sensitive temperature thresholds during the rapid thermal quench. As the local gas temperature falls through successive activation energy barriers, specific forward and reverse reaction steps become sequentially dormant because the remaining thermal energy can no longer sustain the required molecular collision rates or transition state transitions. This step-by-step kinetic shut-down progresses continuously until all primary gas-phase chemistry completely locks into place below a definitive threshold of 500 K. Below this critical thermal boundary, the molecular configuration becomes entirely frozen, effectively halting all further gas-phase radical propagation, recombination, or abstraction steps, and ensuring that the chemical composition captured at this point remains unchanged as it moves further downstream.

The realistic predictability of the model improves dramatically when moving beyond single-phase constraints, as explicitly accounting for heterogeneous solid carbon precipitation shifts the downstream reaction pathways and ultimate product profiles significantly away from pure gas-phase baselines. Introducing a condensed carbon phase allows a massive portion of the volatile carbon mass to rapidly drop out of the gaseous stream as solid soot structures, heavily depleting the remaining volatile mixture of its primary carbon building blocks. In this carbon-depleted, hydrogen-rich environment, the active chemical pathways change completely during the thermal drawdown, steering the system away from the heavy accumulation of unsaturated species. Instead of yielding high concentrations of acetylene, the altered radical chemistry actively converts the residual gas-phase intermediates into stable ethane and unreacted methane, demonstrating that physical phase changes fundamentally redirect gas-phase chemical mechanisms.

Finally, to make these highly complex, multi-phase, and multi-dimensional simulations computationally viable for advanced engineering design and integration, a rigorous Principal Component Analysis mechanism reduction framework was successfully deployed. This eigenvalue-driven optimization process evaluated the global rate-of-production sensitivity matrix, allowing researchers to systematically identify, isolate, and trim non-essential reaction steps and multi-collinear pathways without disrupting the core chemical network. This systematic simplification trimmed the dense baseline reaction network down to a highly compact scheme consisting of exactly 102 irreversible reactions. By drastically reducing the stiff ordinary differential equation overhead, this lean mechanism successfully accelerated computational processing speeds by a remarkable 61-fold, while simultaneously maintaining a strict 0.1% predictive accuracy relative to the original, unreduced full kinetic mechanism.

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