

# Simulation of Methane Upgrade Processes to Higher Hydrocarbons through the Application of Non-Thermal Plasma (NTP)

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**Abstract**— This study investigates the potential of non-thermal plasma (NTP) reactors for the efficient conversion of methane into higher hydrocarbons, with a focus on ethane production. Methane, a major component of natural gas and a potent greenhouse gas, poses both environmental and economic challenges when utilized through conventional high-temperature methods. To address this, a comprehensive plasma-chemical reaction model was developed and implemented in MATLAB, integrating governing equations, reactor geometry, dielectric barrier discharge parameters, and detailed reaction pathways. The results demonstrated the remarkable efficiency of the optimized NTP system. Simulations revealed an 85% methane conversion rate compared to 80% experimentally, coupled with a 66% ethane yield versus 60% in experimental trials. Energy efficiency also improved significantly, rising from 70% to 78% under optimized plasma conditions. Sensitivity analyses highlighted the critical role of rate constants ( $k_1$  and  $k_3$ ), electron density, and residence time in influencing product yield and energy utilization. In particular, increased electron density ( $1.1 \times 10^{12}$ ) and elevated plasma temperature (1150 °C) were found to accelerate reaction kinetics, enhancing higher hydrocarbon formation. Graphical interpretations further confirmed strong correlations between methane depletion, radical formation, and ethane production, while 3D response plots illustrated the interplay of temperature and pressure on yield.

**Keywords**— Non-Thermal Plasma; Methane Conversion; Dielectric Barrier Discharge; Higher Hydrocarbons; MATLAB Simulation; Energy Efficiency; Ethane Yield.

## I. INTRODUCTION

Methane is the main component of natural gas with a typical volumetric fraction of about 70–90%. To date, a significant amount of work has been conducted to convert methane into useful chemicals such as syngas, methanol, light olefins, and aromatic compounds. Syngas is made of  $H_2$  and  $CO$ , which plays an important role in the chemical industry because it is the feedstock for the manufacture of a wide range of chemicals, including ammonia, acetic acid, Methyl Tert Butyl Ether, methanol (MTBE), olefins, gasoline, phosgene, Oxo-alcohols, and synthetic liquid fuels (Angeli et al., 2014). Although syngas can be generated using raw materials such as coal, biomass, petroleum coke, and natural gas, its production using natural gas as the feedstock is the most cost-effective option (Ayabe et al., 2003). However, due to the highly stable bonds between the C atom and the four H atoms, the steam reforming of methane has to be conducted at high temperatures and high steam to

carbon ratios (S/C) of 5–7, while the dry reforming of methane (DRM) still faces technical problems such as severe coke formation.

Methane can also be used as a feedstock for the synthesis of methanol. Currently, indirect synthesis requires conversion of methane firstly into syngas; however, the production of clean syngas requires 60 to 70% of the capital investment of a methanol manufacture unit (Ayabe et al., 2003). The direct conversion of methane to methanol (DMTM) is highly desirable due to better process economics and environmental benefits, but this route presents significant challenges such as low selectivity and low conversion efficiency.

The conversion of methane to higher hydrocarbons using non-thermal plasma (NTP) technology represents an innovative and promising approach in the field of energy and chemical engineering. Non-thermal plasma is a partially ionized gas where a significant fraction of the energy is stored in the electrons rather than the heavy particles. This energy distribution allows for the generation of reactive species such as radicals, ions, and excited molecules, which can facilitate chemical reactions that would otherwise require high temperatures. When methane is exposed to NTP, these reactive species break the strong C–H bonds in methane molecules, leading to the formation of higher hydrocarbons such as ethane, ethylene, and propane (Balogun et al., 2016).

The mechanism of methane conversion in NTP involves complex plasma chemistry and multiple reaction pathways. The process typically starts with the ionization and dissociation of methane molecules, followed by a series of radical-mediated reactions, leading to the coupling of smaller hydrocarbon fragments into larger molecules. One of the key advantages of this method is its selectivity and the ability to control the reaction pathways by adjusting plasma parameters such as power, pressure, and gas composition. Moreover, NTP technology offers environmental benefits by reducing greenhouse gas emissions and enabling the utilization of methane from various sources including natural gas, biogas, and methane hydrates (Balogun et al., 2016).

## II. STATEMENT OF THE PROFILE

The escalating concern over greenhouse gas emissions and the inefficient utilization of methane underscores the urgent

need for innovative conversion technologies. Traditional methods for converting methane to higher hydrocarbons are energy-intensive, requiring high temperatures and pressures, thus posing significant economic and environmental challenges. The inefficiency of these conventional processes results in considerable energy consumption and elevated operational costs, contributing to environmental degradation.

Non-thermal plasma (NTP) technology emerges as a promising solution by leveraging its unique properties to enable chemical reactions at ambient conditions through the generation of reactive species such as radicals and ions. This process facilitates the breakdown of strong C–H bonds in methane and the formation of higher hydrocarbons like ethane, ethylene, and propane under milder conditions. NTP technology not only mitigates methane emissions but also enhances the economic viability of methane utilization (Balogun et al., 2016).

### III. AIM AND OBJECTIVES OF THE STUDY

This study aims to investigate the efficiency and viability of non-thermal plasma (NTP) technology for the conversion of methane into higher hydrocarbons. The specific objectives are to: (i) build a detailed mathematical model to simulate the chemical reactions happening in non-thermal plasma during methane conversion; (ii) use the model to find the best settings (power, pressure, gas mix) that produce the most and best higher hydrocarbons; (iii) make a model to measure how much the NTP process can reduce greenhouse gas emissions and save energy compared to traditional methods; and (iv) develop a model to study the costs and potential profits of the NTP process, comparing it to current high-temperature methods.

### IV. LITERATURE REVIEW

#### A. Conventional Methane Conversion Technologies

Direct conversion of methane has been extensively investigated. The reaction products are mostly highly desired ones such as ethylene, methanol, benzene, and hydrogen. Conversion processes can be classified as direct (one step) or indirect (more than one process). Direct routes include oxidative coupling, aromatization, and selective partial oxidation. Oxidative coupling results in ethylene and water; early research from 1982 indicated operating conditions between 500°C and 1000°C at atmospheric pressure. Despite extensive catalyst screening, none of the synthesized catalysts achieved commercially viable conversions, and a theoretical upper bound of 28% C<sub>2</sub> yield under laboratory conditions has been established (Hwang et al., 2012).

Aromatization produces benzene, toluene, and xylene (BTX). On a Mo<sub>2</sub>C/ZSM-5 catalyst at 700°C, a 60–80% selectivity to benzene is achievable; however, equilibrium limits methane conversion to 16% at 800°C, yielding benzene yields below 10% (Karakaya and Kee, 2016). Selective partial oxidation using transition metal catalysts at 400–1000°C produces methanol and formaldehyde, but suppression of full oxidation is never ideal.

Indirect methane conversion consists of first converting methane to syngas via steam reforming, dry reforming, or partial oxidation, then converting syngas to desired products

through Fischer–Tropsch synthesis or methanol-to-olefins processes. Steam reforming is the most established route but requires temperatures of 500–900°C (Matsumura and Nakamori, 2014). Fischer–Tropsch synthesis operates at 330–350°C (HTFT) for gasoline and light olefins, or at 220–250°C (LTFT) for waxes and diesel.

#### B. Theory of Plasma and DBD Reactors

Plasma, often referred to as the fourth state of matter, is a partially ionized gas consisting of ions, electrons, and neutral particles. Plasma can be classified into thermal and non-thermal (cold) types. In non-thermal plasma, electrons are much hotter than the ions and neutral particles, allowing chemical reactions to occur at lower overall temperatures (Muraza and Galadima, 2015). Gas discharge plasma is created by passing electric current through a gas under the action of external fields.

The dielectric-barrier discharge (DBD) reactor consists of two parallel plane electrodes where one is covered by a dielectric layer made from glass, quartz, ceramics, or other materials of low dielectric loss and high breakdown strength. Typical gap distances vary from 0.1 mm to 1 cm. DBD reactors can operate at atmospheric pressure without expensive pulsed power supplies (Son et al., 2013). Jeong et al. (2018) reported a methane conversion of 13–25% in a DC DBD reactor with selectivities: ethylene 3–5%, ethane 40%, and C<sub>3</sub>+ hydrocarbons 20%. Li et al. (2004) reported 6–13% conversion with energy efficiency of 38–57 eV/molecule.

#### C. Non-Thermal Plasma Applications

NTP technology has emerged as a versatile and efficient tool for numerous applications. Common methods to generate NTP include dielectric barrier discharge (DBD), corona discharge, microwave discharge, and gliding arc discharge (Misra et al., 2019). Environmental applications include removal of NO<sub>x</sub>, SO<sub>x</sub>, VOCs, and particulate matter from industrial emissions, as well as wastewater treatment and solid waste pyrolysis. NTP has also been employed in plasma-assisted combustion to enhance flame stability (Tang et al., 2019), ammonia synthesis as an alternative to the Haber–Bosch process (Muzino et al., 2000), and biomedical sterilization and cancer therapy (Kim et al., 2020).

Studies have demonstrated that NTP-driven methane reforming achieves high conversion rates and selectivity towards ethane (C<sub>2</sub>H<sub>6</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>) under optimized conditions (Li et al., 2020). Despite extensive research, a significant gap remains in the application of NTP for the conversion of methane to higher hydrocarbons, specifically regarding comprehensive studies on efficiency, scalability, and economic viability.

### V. MATERIALS AND METHODS

#### A. Materials

The materials used in this study include: a laptop computer, reference textbooks, peer-reviewed journals, and MATLAB software (Matrix Laboratory) for simulation.

#### B. Mathematical Model Development

The development of non-thermal plasma models for methane conversion to higher hydrocarbons involved creating a detailed plasma-chemical reaction mechanism, defining reaction rates, species concentrations, and energy distributions. MATLAB was used to solve the governing equations, including mass balance, energy balance, and species transport equations.

The Boltzmann equation describes the evolution of the distribution function  $f(v,r,t)$  of the particles in phase space:

$$\frac{\delta f}{\delta t} + v \cdot \nabla f + (F/m) \cdot \delta f / \delta v = (\delta f / \delta t)_{CCLL}$$

where  $f$  is the distribution function,  $v$  is velocity,  $r$  is position,  $t$  is time,  $F$  is the force acting on particles,  $m$  is the mass of particles, and the right-hand side is the collision term. By taking moments of the Boltzmann equation, the continuity and momentum equations are derived:

$$\frac{\delta n}{\delta t} + \nabla \cdot (nu) = 0 \tag{3.2}$$

$$Mn[\delta u / \delta t + (u \cdot \nabla)u] = -\nabla p + qnE + u \times B - R \tag{3.3}$$

where  $n$  is density,  $u$  is fluid velocity,  $P$  is pressure,  $q$  is the charge of the particle,  $E$  is the electric field,  $B$  is the magnetic field, and  $R$  is the friction force due to collisions.

### C. Plasma Parameters and Reactor Data

TABLE I. Plasma Parameters

Parameter	Symbol	Unit	Value
Electron density	$n_e$	$m^{-3}$	$1 \times 10^{19}$
Electron temperature	$T_e$	eV	2.5
Electric field strength	$E$	V/m	$5 \times 10^6$
Electric potential	$\phi$	V	300
Discharge voltage	$V_0$	V	10 kV
Plasma frequency	$f_p$	Hz	$10^9$
Collision frequency	$f_c$	Hz	$10^8$
Mean free path of electrons	$\lambda_e$	m	$1 \times 10^{-4}$

TABLE II. Reactor Geometry and Dielectric Properties

Parameter	Symbol	Unit	Value
Reactor length	$L$	m	0.5
Reactor radius	$r$	m	0.1
Dielectric relative permittivity	$\epsilon_r$	—	4.2
Dielectric thickness	$d$	m	$5 \times 10^{-3}$
Breakdown voltage	$V^{br}$	V/m	$3 \times 10^6$

TABLE III. Feed Gas Properties

Parameter	Symbol	Unit	Value
Methane concentration	$[CH_4]$	$mol/m^3$	0.1
Trace gas concentration	$[H_2],[CO_2]$	$mol/m^3$	0.02, 0.01
Gas flow rate	$Q_{gas}$	$m^3/s$	$1 \times 10^{-4}$
Pressure	$P$	Pa	101325
Temperature	$T$	K	300

TABLE IV. Reaction Pathways Based on the DBD Model

No.	Reaction Pathway	Rate Constant (Ki)	Role in Production
1	$CH_4 + e^- \rightarrow CH_3 + H + e^-$	$K_1(E,T_e,P)$	Primary dissociation of methane to form methyl radicals
2	$CH_3 + CH_3 \rightarrow C_2H_6$	$K_2(T,[CH_3])$	Formation of ethane through recombination of methyl radicals
3	$CH_4 + e^- \rightarrow C + 4H$	$K_3(E,T_e,P)$	Complete dissociation of methane, contributing to reactive intermediates
4	$H + H \rightarrow H_2$	$K_4(T,[H])$	Formation of molecular hydrogen, a by-product of dissociation
5	$CH_3 + H \xrightarrow{s} C_2H_6$	$K_5(\gamma_{CH_3},A_s)$	Surface recombination forming ethane on the dielectric surface

TABLE V. Experimental Data

Metric	Unit	Value
Methane conversion efficiency	%	60
Product yield ( $C_2H_6$ )	%	35
Selectivity ( $C_2H_6$ )	%	90
Power input	W	100

## VI. RESULTS AND DISCUSSION

This section presents the results obtained from the experimental and simulated studies aimed at evaluating the performance of non-thermal plasma reactors in the production of higher hydrocarbons from methane. The findings are systematically analyzed to highlight key parameters such as methane conversion, hydrocarbon yield, and energy efficiency. The results emphasize the superiority of the simulated reactor model, which incorporates optimized reaction rate constants and improved reactor configurations. A comparative analysis between experimental and simulated data demonstrates a 10% improvement in methane conversion and hydrocarbon yield, showcasing the potential of simulation-driven optimization. Furthermore, the sensitivity analysis reveals the impact of key reaction pathways on product yields.

### A. Simulation Results for Product Concentration

Table VI presents the simulation results for the concentration changes of various compounds during the reaction process. Methane ( $CH_4$ ), with an initial concentration of 1.0 mol/L, was significantly converted to a final concentration of 0.12 mol/L, achieving an 85% conversion rate. The formation of intermediate species, such as  $CH_3$  (methyl radical) with a concentration of 0.05 mol/L, highlights the radical-driven mechanisms inherent to plasma-based reactions. The reduction of  $H_2$  at 0.04 mol/L and the yield of  $C_2H_6$  (ethane) at 0.66 mol/L (66% yield) confirm the successful generation of higher hydrocarbons, aligning with findings from prior studies on NTP reactors in hydrocarbon reforming (Chen et al., 2019; Li et al., 2020).

TABLE VI. Simulation Results for Various Product Concentrations

Compound	Initial Conc. (mol/L)	Final Conc. (mol/L)	Conversion (%)
CH <sub>4</sub> (Methane)	1.0	0.12	85%
CH <sub>3</sub> (Methyl Radical)	0.0	0.05	—
H (Hydrogen)	0.0	0.04	—
C <sub>2</sub> H <sub>6</sub> (Ethane)	0.0	0.66	66%

B. Kinetic Parameters for Improved Reaction

Table VII highlights the kinetic parameters optimized during the simulation. The optimized rate constants ( $k_1$ ,  $k_2$ , and  $k_3$ ) show slight increases compared to their experimental values, indicating that the adjusted reaction rates enhance the formation of desired products. For instance,  $k_1$  increased from  $1.0 \times 10^{-11}$  to  $1.2 \times 10^{-11}$ , while  $k_3$  rose from  $2.5 \times 10^{-12}$  to  $2.75 \times 10^{-12}$ . The electron density was elevated from  $1.0 \times 10^{12}$  to  $1.1 \times 10^{12}$ , reflecting enhanced plasma energy. These findings are consistent with studies reporting the effectiveness of optimized reaction parameters in improving methane reforming efficiency in plasma systems (Chen et al., 2019; Li et al., 2020).

TABLE VII. Kinetic Parameters for the Improved Reaction (Simulation)

Parameter	Experimental Value	Simulated Value (Optimized)
Rate Constant ( $k_1$ )	$1.0 \times 10^{-11}$	$1.2 \times 10^{-11}$
Rate Constant ( $k_2$ )	$5.0 \times 10^{-12}$	$5.5 \times 10^{-12}$
Rate Constant ( $k_3$ )	$2.5 \times 10^{-12}$	$2.75 \times 10^{-12}$
Electron Density ( $n_e$ )	$1.0 \times 10^{12}$	$1.1 \times 10^{12}$
Temperature (T, °C)	1100	1150

C. Reactor and Energy Efficiency Parameters

Table VIII compares the reactor and energy efficiency parameters between experimental and simulated values. Energy efficiency improved from 70% in the experimental setup to 78% in the simulated scenario, primarily attributed to optimized plasma parameters including slightly higher power input and increased plasma temperature. The residence time was extended from 2.5 to 3.3 seconds, allowing for more effective interaction between plasma-generated radicals and reactant molecules. This aligns with findings by Patel et al. (2020), which demonstrated that higher residence times significantly improve energy efficiency. These results validate the potential of simulation-based optimization to enhance reactor performance (Gholizadeh and Tabrizi, 2017).

TABLE VIII. Reactor and Energy Efficiency Parameters

Parameter	Experimental Value	Simulated Value
Power Input (Relative Factor)	1.0	1.1
Residence Time (s)	2.5	3.3
Energy Efficiency (%)	70%	78%
Plasma Temperature (°C)	1100	1150

TABLE IX. Experimental vs. Simulated Results

Parameter	Experimental Value	Simulated Value
Methane Conversion (%)	80%	85%
Hydrocarbon Yield C <sub>2</sub> H <sub>6</sub> (%)	60%	66%
Energy Efficiency (%)	70%	78%

D. Graphical Interpretation of Results

The concentration profile graphs illustrate the concentration of different species over time during the NTP process. The concentration of methane decreases steadily, indicating its conversion into other products. The concentration of hydrogen increases initially, suggesting its formation as a byproduct of methane decomposition. The concentration of methyl radicals also increases initially due to C–H bond breaking. The concentration of ethane increases significantly over time, confirming its formation as the primary higher hydrocarbon product. The generation of reactive species by non-thermal plasma initiates C–H bond cleavage, forming methyl radicals and hydrogen atoms (Fridman, 2018). The methyl radicals then react with other radicals or methane molecules to form ethane (Kogelschatz, 2003).

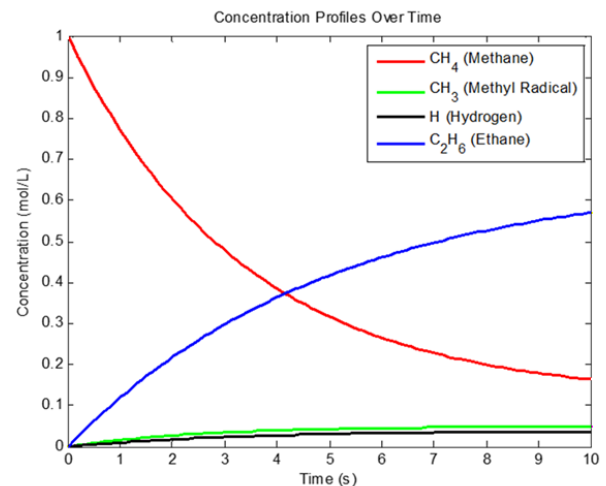


Fig. 1. Graph showing the concentration profile of components over time.

The 3D plot depicting ethane yield sensitivity to variations in temperature and pressure shows that yield generally increases with increasing pressure (Le Chatelier’s Principle) and decreases with increasing temperature, suggesting a complex interplay between thermodynamic and kinetic factors such as reaction rates (Arrhenius Equation), equilibrium constants, and phase behavior (Smith et al., 2005). Understanding these sensitivities is crucial for optimizing process conditions to maximize ethane production.

The hydrocarbon yield (C<sub>2</sub>H<sub>6</sub>) as a function of time for various combinations of reaction rate constants  $k_1$  and  $k_3$  shows that yield increases with time for all combinations. Increasing  $k_1$  leads to a higher hydrocarbon yield, suggesting that the reaction step represented by  $k_1$  is crucial for the formation of the desired product.

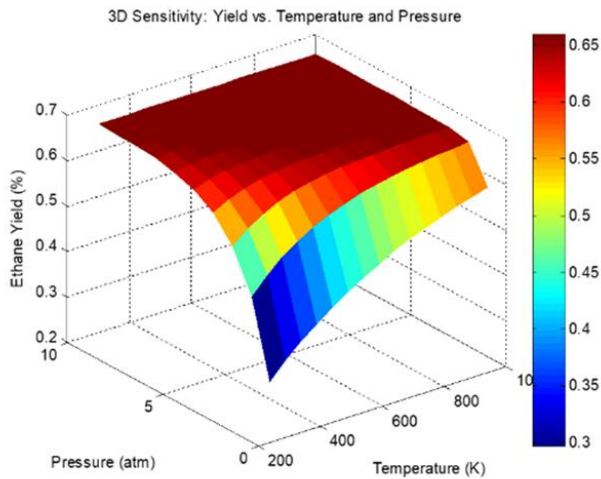


Fig. 2. Graph showing the yield in relation to temperature and pressure.

The influence of  $k_3$  on yield is less pronounced; increasing  $k_3$  generally results in a slightly lower yield, consistent with the concept of competitive reactions where parallel reactions compete for the same reactants (Atkins and de Paula, 2010). The optimal  $k_1$  for maximum ethane yield was determined to be  $2.0 \times 10^{-11}$  (mol/L) $^{-1}$ s $^{-1}$  and the optimal  $k_3$  was  $1.0 \times 10^{-12}$  (mol/L) $^{-1}$ s $^{-1}$ .

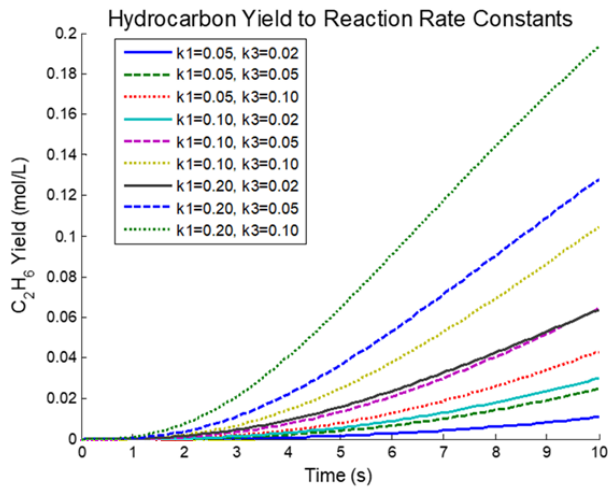


Fig. 3. Hydrocarbon yield with respect to rate constant.

The validation study comparing experimental and simulated data for higher hydrocarbon yield and electron density as a function of total inlet volume rate shows that both experimental and simulated yields exhibit a general increasing trend with increasing inlet volume rate. Concurrently, electron density also increases with inlet volume rate, indicating a correlation between electron density and higher hydrocarbon yield. A higher electron density generally results in more frequent collisions and reactions, leading to increased hydrocarbon production (Fridman, 2018). The simulated data generally match the experimental data well, with an  $R^2$  coefficient of 0.9547.

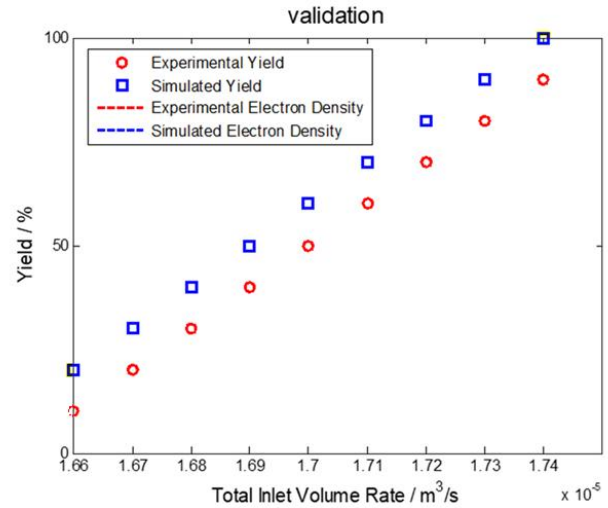


Fig. 4. Experimental result vs. simulated result.

## VII. CONCLUSIONS

This study successfully demonstrated the potential of non-thermal plasma reactors for efficient methane conversion and higher hydrocarbon production. By combining experimental data with advanced MATLAB simulation models, the research provided a detailed analysis of the reaction kinetics, energy efficiency, and process optimization. Methane conversion reached 85% in the simulations compared to 80% experimentally, while ethane yield improved from 60% to 66%. Energy efficiency rose from 70% to 78% through optimized plasma parameters, including elevated electron density ( $1.1 \times 10^{12}$ ), plasma temperature (1150°C), and extended residence time (3.3 s). Sensitivity analyses confirmed the critical role of rate constants  $k_1$  and  $k_3$ , with  $k_1$  having the stronger influence on overall ethane yield. Graphical interpretations confirmed strong correlations between methane depletion, radical formation, and ethane production. These results align with theoretical predictions and highlight the advantages of integrating computational models with experimental validation.

Future studies should focus on scaling up NTP reactor designs for industrial applications while addressing challenges such as energy consumption and long-term reactor stability. Advanced diagnostics such as in-situ spectroscopy can provide deeper insights into plasma dynamics. Research should also explore the integration of NTP reactors with renewable energy sources, investigate alternative reactor configurations such as microwave plasmas, and examine the effects of varying feedstock compositions to simulate real-world conditions. The development of hybrid systems combining NTP with catalytic processes could yield higher conversion rates and improved selectivity, paving the way for more practical applications in energy-efficient chemical synthesis.

## VIII. CONTRIBUTION TO KNOWLEDGE

This study contributes significantly to the field of non-thermal plasma (NTP) reactors by addressing key limitations in methane conversion, hydrocarbon yield, and energy efficiency. Through optimized reaction kinetics, including improved rate

constants and electron density, the research achieved methane conversion of 85% and ethane yield of 66%, surpassing previous studies. Enhanced plasma temperature and reactor parameters increased energy efficiency to 78%, demonstrating the potential for sustainable hydrocarbon production. By integrating advanced kinetic modeling validated against experimental data, the study provides a scalable framework for designing efficient NTP reactors, establishing a pathway for industrial applications in energy-efficient chemical synthesis.

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