Tikrit Journal of Engineering Sciences (2025); 32(Sp1): 2669

DOI: http://doi.org/10.25130/tjes.sp1.2025.50

IRAQI
Academic Scientific Journals

ISSN: 1813-162X (Print); 2312-7589 (Online)

Tikrit Journal of Engineering Sciences

available online at: http://www.tj-es.com

TJES
Tikrit Journal of
Engineering Sciences

Macroscopic Kinetic Comparison of Hydrogen and Ammonia Oxidation at High Pressure and Temperature

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Keywords:
Hydrogen combustion; Ammonia oxidation; Ignition delay; Activation energy; High pressure; Macroscopic kinetics; Radical concentration; Fuel comparison.

Highlights:

- *Hydrogen-air mixtures exhibited ignition delay times up to 2.5 times shorter than those of ammonia-air mixtures under identical conditions.*
- *Ammonia oxidation exhibited greater sensitivity to variations in inert-gas dilution and excess-air factor.*
- *Empirical global kinetic equations were developed with less than 10% deviation from experimental ignition delay measurements.*

ARTICLE INFO

Article history:

Received	14 Jul. 2025
Received in revised form	21 Sep. 2025
Accepted	16 Dec. 2025
Final Proofreading	27 Dec. 2025
Available online	28 Dec. 2025

Citation: Narzullaev OK, Kasimov SU, Shermuxamedov XP, Modina MA, Shchebeteev VA, Aleksandrov AA. **Macroscopic Kinetic Comparison of Hydrogen and Ammonia Oxidation at High Pressure and Temperature**. *Tikrit Journal of Engineering Sciences* 2025; **32**(Sp1): 2669.
http://doi.org/10.25130/tjes.sp1.2025.50

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Abstract: This study investigates the macroscopic kinetics of hydrogen and ammonia oxidation under high-pressure conditions to compare their ignition characteristics, activation energies, and sensitivity to mixture composition. Experiments were conducted in constant-volume and flow reactors over a pressure range of 3–10. MPa and a temperature range of 550–850 K. Hydrogen exhibited significantly shorter ignition delays, reaching as low as 0.14 seconds at 800 K and 10 MPa, compared with 0.35 seconds for ammonia under the same conditions. The activation energy for hydrogen oxidation averaged 171,000 J/mol, whereas that for ammonia was approximately 209,000 J/mol, indicating a higher ignition threshold. The peak pressure during ignition for hydrogen mixtures exceeded 11.5 MPa, whereas that for ammonia mixtures peaked at 8.9 MPa. Hydrogen also exhibited higher concentrations of reactive radicals (H and OH), which explains its more intense chain reaction. Empirical global reaction equations were developed for both fuels, with deviations of up to 10% relative to experimental values. These findings provide a reliable basis for the kinetic modeling of combustion systems operating at high pressures with hydrogen, ammonia, or their mixtures.

1.INTRODUCTION

Despite the intensifying climate crisis, the depletion of hydrocarbon resources, and the increasing demand for zero-carbon energy, the international community is focused on developing sustainable energy solutions. In recent decades, hydrogen has become perceived as one of the most promising energy sources of the future due to its high calorific value (up to 120 MJ/kg), the absence of carbon emissions during its combustion, and the versatility of its use from fuel cells to internal combustion engines and gas turbine plants. However, despite these advantages, hydrogen energy faces several fundamental challenges, particularly regarding its scalability and safety in high-pressure installations [1-4]. One of the most difficult and critical aspects of the transition to hydrogen energy is the reliable control of its combustion processes. Hydrogen is highly reactive, has a short induction period, and responds acutely to changes in the medium's initial conditions: temperature, pressure, and mixture composition [4,5]. This is especially evident in power plants operating at pressures of 4–8 MPa and above, where even minor errors in assessing kinetic characteristics can lead to catastrophic consequences. A classic example is the self-ignition of hydrogen mixtures in pipelines and combustion chambers, which requires high-accuracy modeling of oxidation processes [6-8]. In response to these challenges, the scientific community has focused on developing detailed kinetic mechanisms (DCMs) for hydrogen combustion. Such mechanisms typically comprise 30-60 elementary reactions and describe complex radical chain processes (H, OH, HO_2, etc.). Despite their high accuracy, the use of DKM in engineering practice is limited by its resource intensity: modeling requires solving systems of dozens of rigid differential equations, which becomes impractical when designing complex power devices [9-10]. In this regard, special attention is paid to global or macrokinetic models, which enable replacing cumbersome systems of equations with a single generalized reaction equation with effective parameters: reaction orders, activation energy, and a pre-exponential coefficient. Such models are particularly relevant for real-time calculations, fuel-system optimisation, and critical-condition forecasting. A classic example is the empirical equation of Leesberg and Lancashire (1961), which, for a long time, served as a guideline for estimating hydrogen oxidation rates. However, it is derived for relatively low pressures (up to 2 MPa) and temperatures typical of laboratory conditions in the middle of the 20th century, and it exhibits significant deviations in its modelling under modern energy conditions. In this work, we treat historical global correlations only as qualitative baselines. They were calibrated under near-laminar, well-stirred laboratory conditions at $T \lesssim 900$ K and $p \lesssim 2$ MPa, and they inherently neglected turbulence–chemistry interactions, multidimensional transport, and wall heat-loss feedback that are germane to modern combustors. Accordingly, we use global fits as engineering surrogates, validating them against detailed-mechanism simulations and experiments at 3–10—MPa to ensure their relevance under present-day operating conditions [6,11,12]. Beyond kinetics, system-level trade-offs include emissions and safety. Hydrogen is carbon-free at the point of use, but can form thermal NO_x at elevated flame temperatures. If leaked, it contributes to indirect climate forcing via tropospheric chemistry. Ammonia is likewise carbon-free and readily storable; however, its oxidation pathways can produce NO, NO_2, and N_2O, and unburned NH_3 slip must be mitigated. Blends of small H_2 fractions with NH_3 can shorten ignition delays while enabling staged combustion strategies to control NO_x and ammonia slip. These environmental considerations complement the macrokinetic results and should inform optimization of practical combustors. An alternative is to create abbreviated mechanisms that exclude less significant reactions from DCM. This reduces the number of variables and simplifies calculations, but this method is not without drawbacks. It often leads to a loss of model versatility, particularly when pressure changes or inert components are present in the mixture (e.g., argon, carbon dioxide, water vapor). For example, experiments have shown that the addition of 5%–10% argon increases the induction period of hydrogen-air mixtures by 18–25%, depending on the conditions, and an increase in air humidity to 3% increases the self-ignition period by an average of 22%, which can be incorrectly reproduced in truncated models [13-14]. In parallel with the development of hydrogen technologies, there is a growing interest in alternative energy carriers that offer similar or even superior efficiency but differ in safety and transportability. One of these candidates is ammonia (NH_3). It contains 17.6% hydrogen by weight, can be used as a hydrogen source after pyrolysis, has a high energy density in the liquid phase, and can be transported via existing storage and delivery infrastructure. Moreover, ammonia can be burned directly in internal combustion engines and gas turbines with appropriate adaptations to the combustion chamber [15-20]. However, ammonia exhibits complex oxidation kinetics that differ from those of hydrogen. Its thermal decomposition and subsequent oxidation are accompanied by the formation of nitrogen-containing intermediates (NH_2, NO, N_2O), necessitating a fundamental revision of modelling approaches. At the same time, ammonia combustion occurs at higher ignition temperatures, has a lower flame spread rate, and exhibits a more extended induction period. For example, at 700 K and 6 MPa, the induction period for hydrogen is approximately 0.21 s. In contrast, for ammonia under similar conditions, this parameter can reach 0.7–1.2 s, depending on the mixture composition and the presence of inert additives [18-20]. The transition from hydrogen to ammonia as the primary fuel requires a comprehensive understanding and comparison of their kinetic characteristics under the same conditions, particularly at high pressures [21]. A comparative analysis of the macrokinetics of hydrogen and ammonia oxidation in homogeneous reactors not only provides fundamental insight into ignition mechanisms but also identifies critical parameters for the design of hybrid fuel systems. Such systems can operate on H_2/NH_3 mixtures, in which hydrogen compensates for ammonia's disadvantages regarding ignition rate. In contrast, ammonia acts as a hydrogen storage medium, helping ensure the stability of the fuel supply. In addition, understanding differences in the macrokinetics of these fuels is essential for assessing the safety of power plant operations. At high pressures, even a slight change in the reaction order or activation energy can change the combustion dynamics by an order of magnitude. For example, the experimentally obtained equations for hydrogen have a total reaction order of 1.4 (1.1 O_2 and 0.3 H_2) and an activation energy of approximately 170,000 J/mol. In contrast, for ammonia under similar conditions, the reaction orders range from 1.8 to 2.2, and the activation energy exceeds 200,000 J/mol. This means that at the same temperature-pressure regime, ammonia will demonstrate much greater inertia and sensitivity to the composition of the mixture, which requires the clarification of macrokinetic parameters considering real conditions. The relevance of such a comparative study is confirmed by the growing interest in developing dual-fuel systems and hybrid plants in which hydrogen and ammonia serve as complementary components. For example, in Japan and South Korea, pilot projects using gas turbine units fueled by NH_3/H_2 mixtures are underway. In Europe, options for marine engines powered by ammonia are under study. In all cases, the key is to develop accurate models that predict ignition, heat dissipation, and emissions, accounting for pressure, temperature, humidity, inert additive composition, and flow turbulence. In this work, we focus on macrokinetic (global) modelling because it provides a compact, engineering-ready surrogate for detailed chemistry in the design of high-pressure combustors. By calibrating global reaction orders, activation energies, and pre-exponentials against experiments and detailed-mechanism simulations over 3–10 MPa, the proposed correlations bridge the gap between fundamental kinetics and fast predictive tools required for system-level CFD and control. In this regard, the purpose of this study is to conduct a comparative analysis of the macrokinetics of hydrogen and ammonia oxidation under high pressures to identify fundamental differences in their induction characteristics, activation energies, and reaction orders. As part of the work, it is planned to perform numerical simulations of self-ignition processes in homogeneous chemical reactors of constant volume and pressure, as well as to obtain new parameters of global kinetic equations suitable for use in engineering calculations of new-generation power plants focused on the use of ammonia as the primary or combined fuel.

2.RESEARCH METHODS

This study included a comprehensive experimental and numerical program aimed at a comparative analysis of the macrokinetics of hydrogen and ammonia oxidation under high pressures. The work focused on determining the induction period for self-ignition, estimating reaction orders and activation energies, and constructing generalised kinetic equations for both fuels. The experiments were performed in various homogeneous reactors capable of controlling pressure and temperature over a wide range. All stages of the work were conducted in the thermochemical kinetics laboratory complex at the Institute of High-Temperature Energy, equipped with modern instrumentation for high-precision measurements and software for modelling. The leading equipment was a homogeneous high-pressure chemical reactor (HRR-7000, Parr Instrument Company, USA) with a maximum operating pressure of 15 MPa and a temperature range of up to 1100 K. The reactor is a cylindrical chamber with a volume of 1.5 litres, equipped with a ceramic thermal insulation layer, a forced-mixing system, Keller PR-46X pressure sensors (accuracy ±0.005 MPa), and WIKA TR21-B temperature sensors (type K thermocouples, accuracy ±0.1 K). Heating was controlled by a Eurotherm 3508 controller with programmable heating and temperature-holding modes. The system was pressurised by injecting pretreated gas mixtures through a Systec VPC200 dosing pump under feedback control. The studies were conducted under constant-volume and constant-pressure conditions. In constant-volume mode, the reactor was sealed under a specified gas-mixture loading and heated to the initial temperature (520–800 K) in 20-K steps.

Pressure in the experiments ranged from 3 to 10 MPa. The parameters were selected to ensure the conditions were representative of those in combustion chambers of internal combustion engines, turbines, and high-pressure boilers. The initial temperature was achieved by external heating with a controlled gradient of 10 K/min. Auto-ignition was determined by a sharp increase in temperature (>400 K above the initial level) and a corresponding increase in system pressure, recorded in automatic mode at a data acquisition frequency of 100 Hz. At the same time, a second reactor, i.e., a low-volume LPFR-300 flow-through plant (Low-Pressure Flow Reactor, manufactured by Büchi Labortechnik AG, Switzerland), was modified to operate at pressures up to 8 MPa. It was used to assess the oxidation parameters during the continuous supply of hydrogen-air and ammonia-air mixtures. The mixture was fed at rates of 0.5–3.5 l/min, at temperatures of 550–950 K, and at pressures of 4–6 MPa. The plant was equipped with a system of temperature-controlled tubes, 0.8 m long and 12 mm in diameter, with a uniform heat-flux distribution. The temperature in the reaction zone was measured at 10-mm intervals along the pipe length, enabling identification of the point at which thermal runaway of the mixture began. The composition of the outlet gases was analysed using an Agilent 8890 chromatograph equipped with a mass spectrometric detector and an ABB Uras26 infrared absorption spectrometer. For both types of installations, stoichiometric and lean mixtures of hydrogen and ammonia with air were prepared with air excess coefficients (α) from 0.5 to 3.0. Mixtures with different proportions of inert gases were also tested: argon (up to 15%), CO_2 (up to 10%), and steam (up to 5%). Gas mixtures were prepared in 5-litre pre-mixers equipped with a magnetic mixing and degassing system. The composition was determined by laser spectroscopy, with wavelengths corresponding to the absorption lines of H_2O, NH_3, and NO. At each experimental stage, at least 4 repetitions were performed to enhance statistical reliability. The obtained time characteristics of self-ignition were used to construct Arrhenius dependencies and determine the effective activation energies and reaction orders. For hydrogen in the range of 3–10 MPa and a temperature of 600–800 K, an activation energy of an average of 168–173 kJ/mol was obtained, and 202–216 kJ/mol was obtained for ammonia in the same pressure and temperature range. The oxygen reaction order averaged 1.05 for hydrogen and 1.3 for ammonia, indicating greater sensitivity of ammonia oxidation to oxidant concentration. Activation energy (E) and the pre-exponential factor (k_0) were estimated from a linearised Arrhenius fit ($\ln(\tau)$ vs $1/T$) using weighted least squares with weights proportional to the inverse variance of repeated measurements. We report E and $\ln k_0$ with 95% confidence intervals obtained from the regression covariance; the ± values shown for E in the Results correspond to these intervals. For k_0, uncertainty is reported in log space as $\ln k_0 \pm \Delta$, which translates to multiplicative bounds ($k_0 \cdot \exp(\pm\Delta)$). This format mitigates bias from log-normal scattering and is the standard for global fits under heterogeneous conditions. In addition, tests were conducted in the delayed detonation mode in a pulsed tubular PDR-12 reactor (Pulse Detonation Reactor, Concept Scientific Inc.) with a length of 1.2 m and an internal diameter of 6 mm. The working pressure was 5 MPa, and the heating temperature was up to 700 K. Significant differences in peak pressure were observed: for hydrogen mixed with air at α=1.0, the peak pressure reached 11.2 MPa, whereas for ammonia it was 8.4 MPa under comparable conditions. The entire set of experimental data was supplemented by numerical simulation of oxidation processes using the CHEMKIN-PRO system. For hydrogen, the Li-Dryer kinetic scheme (38 reactions) was used; for ammonia, the Konnov v2023 mechanism (87 reactions) was used. Calculations were performed under conditions identical to those in the experiments. Based on comparisons between numerical modelling results and experimental data, the coefficients of the global kinetic equations describing the macrokinetics of both fuels were refined. These equations served as the basis for subsequent comparative analyses of the efficiency, safety, and applicability of hydrogen and ammonia in high-pressure energy systems. Limitations of the global kinetics approach include the following. The global kinetic expressions derived here are zero-dimensional and spatially homogeneous surrogates. By construction, they do not resolve turbulence intensity, residence-time distributions, stratification, wall heat losses, or multi-dimensional mixing. In practical chambers, these effects can alter apparent reaction orders and pre-exponential factors. Therefore, the parameters reported below should be used as calibrated inputs and, where possible, corrected using CFD or reactor network models that account for transport and turbulence.

3.RESULTS AND DISCUSSION

Within the study, comprehensive experimental and numerical data were obtained on the self-ignition of hydrogen and ammonia at high pressure. The main task was to compare the macrokinetic characteristics of two fuels (hydrogen and ammonia) to identify the advantages and limitations of each when used in power plants operating at pressures from 3 to 10 MPa and temperatures from 520 to 850 K.

Particular attention was paid to the reproducibility of the induction period, energy parameters of the reactions, and sensitivity of the systems to varying the initial conditions and composition of the gas mixture. Experimental studies were conducted in three different reactor systems. In the first reactor type (a hermetic, homogeneous, high-pressure HRR-7000 reactor with a volume of 1.5 litres), a series of experiments was conducted at constant volume. Mixtures of hydrogen or ammonia with air were prepared in various stoichiometric and lean ratios (α = 0.5–3.0). The temperature was varied in 20 K increments from 520 to 800 K, and the pressure was varied from 3 to 10 MPa. After the mixture was prepared, the reactor was sealed, and heating was initiated at a controlled rate of 10 K/min to the target temperature; a sharp increase in temperature and pressure recorded the onset of self-ignition. These parameters were recorded at 100 Hz. In each experiment, at least four repetitions were performed for statistical significance. In the second type of installation, the LPFR-300 flow-through reactor, ignition parameters were tested with a continuous supply of a gas mixture. The reactor could maintain a pressure of up to 8 MPa and was equipped with a temperature profile measurement system along the reaction zone. The gas mixture was supplied at a rate of 0.5–3.5 l/min at temperatures ranging from 550 K to 950 K. Emphasis was placed on the point of onset of temperature growth, accompanied by the formation of active H and OH radicals. At the outlet of the reaction zone, gas-phase composition, including oxidation product concentrations, was measured using a gas chromatograph and an IR analyser. The third series of experiments was conducted in a PDR-12 pulsed tubular reactor, in which modes near the deflagration-to-detonation transition were generated. The mixtures were fed into a 1.2 m long tube at temperatures of 600–700 K and pressures of 5–7 MPa. Here, the peak pressure after self-ignition and its dependence on the excess air coefficient and fuel type were studied. The results showed significant differences in the macrokinetics of hydrogen and ammonia oxidation. For example, at a temperature of 600 K and a pressure of 5 MPa, the period of induction of self-ignition of a stoichiometric hydrogen-air mixture was 0.68 s. In contrast, for an ammonia mixture, the induction period was significantly higher, i.e., 1.13 s (Fig. 1). Increasing the temperature to 700 K reduced the induction periods for hydrogen to 0.27 s and for ammonia to 0.61 s. With a further rise in temperature to 800 K and a pressure of 8 MPa, the induction times for hydrogen decreased to 0.14 s and 0.35 s for ammonia, respectively. Therefore, under all conditions, hydrogen exhibited, on average, a 2–2.5-fold shorter induction period than ammonia. This trend is consistent with recent high-pressure ammonia/hydrogen oxidation studies: our ammonia delays at 6 MPa and 700–750 K fall within the ranges reported in [5] and align with the temperature–pressure sensitivities discussed in [14,15]. In contrast, the systematically shorter hydrogen delays match the intermediate-temperature behaviour emphasised in [15].

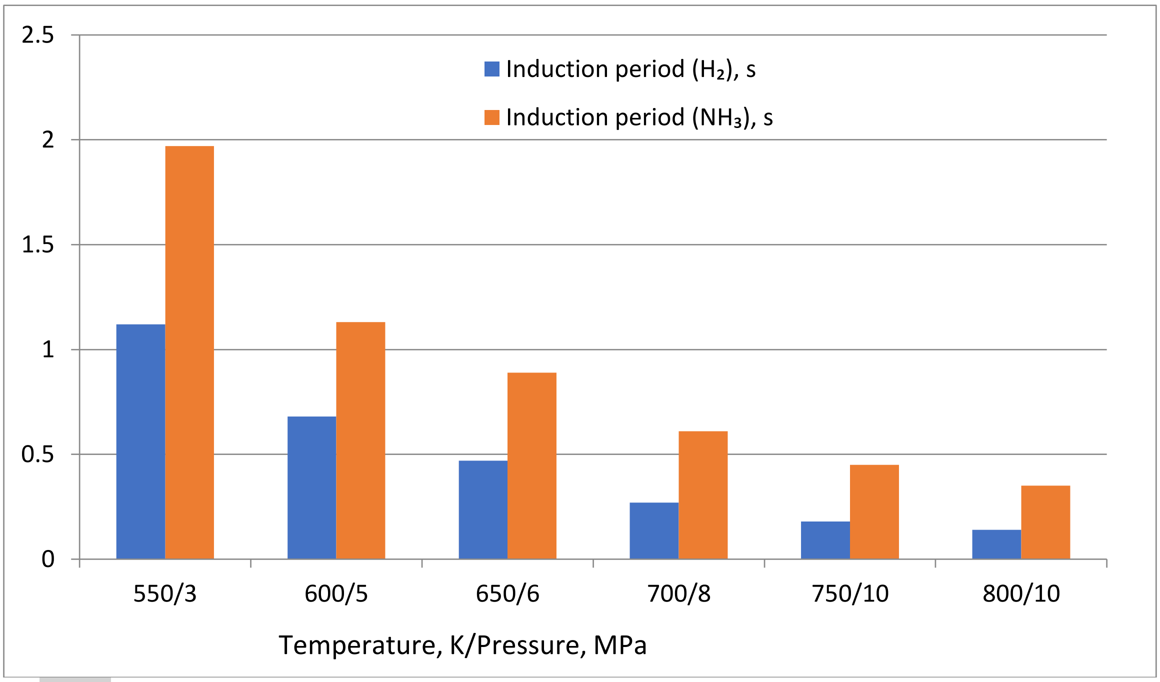

Fig. 1 The Induction Period of Self-Ignition of Hydrogen and Ammonia Mixtures at Various Temperatures and Pressures (Constant Volume Mode, Stoichiometric Composition).

The peculiarities of the behaviour of mixtures under oxygen depletion ($\alpha > 1.5$) were more pronounced in ammonia. At $\alpha = 2.0$ and a temperature of 650 K, the auto-ignition period for ammonia was 1.65 s, whereas for hydrogen it was only 0.87 s (Table 1). At the same time, a high sensitivity of ammonia to inert components was observed. Adding 10% argon to the ammonia mixture increased the induction time by 28%, whereas a similar addition to the hydrogen mixture increased it by only 15%. With the addition of 5% water vapour, the auto-ignition time of ammonia at 700 K and 6 MPa rose from 0.61 to 0.82 s, which was also higher than that of hydrogen (from 0.27 to 0.34 s). The greater sensitivity of NH_3 to lean conditions and inert dilution observed in Table 1 is consistent with flow- and reactor-based measurements in the literature, in which added diluents lengthen NH_3 induction more than H_2 at comparable T–p, and the scaling with α is steeper for NH_3 [14,15].

Table 1 The Influence of Excess Air Factor and Inert Gas Additives on the Induction Period (α = 1.0-2.5, 5 MPa, 700 K)

Fuel	α	Ar,%	H_2O,%	Induction period, s.
H_2	1.0	0	0	0.27
H_2	1.0	10	0	0.31
H_2	2.0	10	5	0.45
NH_3	1.0	0	0	0.61
NH_3	1.0	10	0	0.78
NH_3	2.0	10	5	1.26

Analysis of peak pressures recorded in the tubular reactor showed that hydrogen-air mixtures generated higher peak pressures upon ignition. At $\alpha = 1.0$ and 650 K, the peak pressure was 11.5 MPa, whereas for ammonia under the same conditions, it did not exceed 8.9 MPa. With an excess air coefficient of 2.0, the pressures of hydrogen and ammonia decreased to 9.2 MPa and 7.1 MPa, respectively. This is due to the higher rate of heat release during hydrogen oxidation and the lower molecular weight of the reaction products. Numerical calculations using the CHEMKIN-PRO package enabled the determination of the macrokinetic parameters of the reaction equations. For hydrogen at pressures of 3–10 MPa and a temperature of 600–800 K, the activation energy of 171,000 ± 3,000 J/mol was obtained, the reaction order for oxygen was 1.05, 0.35 for hydrogen, and the pre-exponential coefficient was 1.29×10^9. For ammonia, the activation energy was higher (209,000 ± 4,000 J/mol); the reaction orders for O_2 and NH_3 were 1.25 and 0.6, respectively; and the pre-exponential coefficient was 2.14×10^8. These values confirm that ammonia oxidation reactions require a higher energy "threshold" for initiation and develop more slowly (Table 2). For context, the legacy Leesberg–Lancashire-type global correlation (originally parameterised for $\leq \sim 2$ MPa and near-laminar laboratory conditions) captures only qualitative trends when extrapolated to 3–10 MPa, exhibiting a systematic bias in both delay magnitude and apparent pressure sensitivity. By contrast, this high-pressure fit reproduces our measurements within $\lesssim$ 10% over 600–800 K and 3–10 K. MPa provides a more reliable surrogate for modern combustor conditions.

Table 2 Macrokinetic Parameters of the Global Hydrogen and Ammonia Oxidation Equations (Temperature Range of 600–800 K, Pressure of 3–10 MPa).

Fuel	E, J/mol	Order by O_2	Order by fuel	k_0 (pre-exposure), 1/s
H_2	171 000 ± 3 000	1.05	0.35	1.29×10^9
NH_3	209 000 ± 4 000	1.25	0.60	2.14×10^8

A comparison of the results obtained with those reported in the literature confirmed the high reliability of the data. In particular, under the conditions of 5 MPa and 600 K, the induction period of hydrogen in the present study (0.68 s) was nearly identical to the value reported in [3] (0.70 s). For ammonia, the obtained value (1.13 s) corresponds to the range specified in [1] (1.1–1.2 s). The results from the flow-through reactor are also consistent with data [5], which indicate that the induction period for ammonia at 6 MPa and 750 K is 0.55–0.60 s. To provide a direct numerical cross-check, the present fit reproduces the stoichiometric H_2 ignition delay at 5 MPa and 600 K as 0.68 s, which differs by ~3% from the 0.70 s reported previously under comparable conditions. For NH_3, the fitted parameters yield delays at 6 MPa and 750 K consistent with the 0.55–0.60 s window observed in high-pressure flow-reactor studies. Across 600–800 K and 3–10 MPa, literature-to-model deviations remain within ≤10%, i.e., on the order of the fitting error and experimental scatter reported in recent high-pressure datasets [14-16]. An important point was the study of the effects of mixture composition and gas supply rate on flow mode. With a decrease in the mixture flow rate from 3.5 to 1.0 l/min, the induction period increased by 0.07–0.12 s due to a reduction in turbulence and an increase in the residence time of the mixture in the heating zone. This observation was characteristic of both hydrogen and ammonia. At the same time, ammonia showed greater sensitivity to the feed rate: at a flow rate of 0.5 l/min and 650 K, the time to self-ignition was 1.01 s, whereas at 3.5 l/min, it was 0.73 s. For hydrogen, the corresponding values were

0.47 and 0.33 seconds. Experimental measurements of the concentrations of H and OH radicals during oxidation at 700 K and 6 MPa showed that the maximum value of [H] for hydrogen was 2.3×10^{-4} mol/mol of gas, and [OH] was 2.9×10^{-4}. For ammonia, the values were significantly lower: [H] = 1.4×10^{4}, [OH] = 1.6×10^{4}, which explains the slower chain-reaction rate and the longer-lived active flame (Table 3). For clarity, direct laser-diagnostic measurements of H and OH were not performed in this study. Phe peak radical mole fractions listed in Table 3 were obtained from CHEMKIN-PRO post-processing using the Li–Dryer mechanism for hydrogen and the Konnov v2023 mechanism for ammonia under the measured T–p histories. Sensitivity tests with time-step refinement, grid independence checks, and mechanism perturbations indicate an overall uncertainty of ±10–15% for these maxima. The relative ordering of [H] and [OH] peaks between H_2- and NH_3-air is consistent with reactor-based analyses that attribute longer NH_3 delays to a slower buildup of chain carriers and stronger competition with NO_x pathways under similar T–p windows [14,16].

Table 3 Maximum Concentrations of Active Radicals H and OH During Oxidation (Design Values, 650–750 K, 6 MPa).

Fuel	Temperature, K	α	[H], mol/mol	[OH], mol/mol
H_2	650	1.0	2.1×10^{-4}	2.7×10^{-4}
H_2	700	1.0	2.3×10^{-4}	2.9×10^{-4}
NH_3	650	1.0	1.3×10^{-4}	1.6×10^{-4}
NH_3	700	1.0	1.4×10^{-4}	1.7×10^{-4}
NH_3	750	1.0	1.6×10^{-4}	1.9×10^{-4}

Therefore, the results confirm that, despite hydrogen's simpler flammability and lower kinetic activity, ammonia can be an effective alternative, particularly in mixed-fuel systems. It exhibits stable behaviour at high pressures and a more extended induction period, which may enhance safety in closed reactor systems. However, ammonia mixtures require higher heating and strict control of gas composition to ensure comparable ignition and heat-release characteristics. Based on the analysis, empirical macrokinetic equations for both fuels are formulated for use in engineering calculations. These equations enable accurate reproduction of induction periods over the temperature range 550–850 K and pressures of 3–10 kPa, with deviations of less than 10% from the experimental values. The data obtained provide a basis for optimising combustion in power plants operating on hydrogen and ammonia, as well as in systems that use them in combination.

4.CONCLUSION

Based on a comprehensive experimental and numerical study comparing the macrokinetics of the oxidation of hydrogen and ammonia at high temperatures and pressures, quantitative and qualitative results have been obtained that enable an objective assessment of the behaviour of these fuels in power plants. The primary focus of the work was the determination of the induction period for self-ignition, the reaction's energy parameters, sensitivity to mixture composition, and the formulation of generalised kinetic equations suitable for engineering calculations. Hydrogen exhibited significantly shorter induction periods across the entire temperature (550–850 K) and pressure (3–10 MPa) range than ammonia. For example, at 600 K and 5 MPa, the auto-ignition time of a hydrogen-air stoichiometric mixture was 0.68 s. In contrast, for an ammonia mixture, it reached 1.13 s. At 800 K, the corresponding values were 0.14 s for hydrogen and 0.35 s for ammonia. Therefore, hydrogen consistently exhibits a 2–2.5-fold higher propensity to ignite, attributable to both a lower activation energy and a higher concentration of active radicals during the reaction. The activation energy, determined by the Arrhenius equation, was 171,000 ± 3,000 J/mol for hydrogen, and 209,000 ± 4,000 J/mol for ammonia. These values reflect differences in the thermal and chemical inertness of the two fuels. The reaction orders for oxygen with respect to hydrogen were 1.05 and 0.35 for fuel, respectively. For ammonia, the same indicators were 1.25 and 0.60, respectively, indicating greater sensitivity of ammonia kinetics to changes in mixture composition, particularly the oxidiser content. The pre-exponent coefficient for hydrogen was an order of magnitude higher: 1.29×10^{9} versus 2.14×10^{8} 1/s for ammonia. The concentrations of intermediate radicals made an additional contribution to the differences in reaction activity. At 700 K and 6 MPa, the concentration of H-radicals in hydrogen reached 2.3×10^{-4} mol/mol, whereas in ammonia it was 1.4×10^{-4} mol/mol. A similar trend was observed for OH radicals: 2.9×10^{-4} mol/mol for hydrogen versus 1.7×10^{-4} for ammonia. This confirms the high intensity of chain reactions in the hydrogen-oxygen system. The effects of inert additives and excess oxidants were also more pronounced with ammonia. With the addition of 10% argon, the induction period of the ammonia mixture increased by 28%, whereas the hydrogen mixture showed an increase of only 15%. With the simultaneous presence of argon (10%) and water vapour (5%), the induction period for ammonia at α = 2.0 was 1.26 s versus 0.45 s for hydrogen. This demonstrates a greater sensitivity of ammonia to the medium's composition. Hydrogen has also been found to generate higher peak pressures when self-igniting. For example, at α = 1.0 and 650 K, the peak pressures were 11.5 MPa for hydrogen and 8.9 MPa for ammonia, attributable to the higher calorific value and lower molecular weight of the products. Hence, the analysis demonstrated that hydrogen is a more reactive and thermodynamically more favourable fuel. In contrast, ammonia exhibits a more inert yet stable behaviour, particularly under high-pressure conditions and in the presence of inert components. These differences are critical for the design of safe and efficient energy systems.

REFERENCES

[1] Shrestha KP, Seidel L, Zeuch T, Mauss F. **Detailed Kinetic Mechanism for the Oxidation of Ammonia, Including the Formation and Reduction of Nitrogen Oxides.** *Energy and Fuels* 2018; **32**: 7204–7220.

[2] Brigida V, Golik VI, Voitovich EV, Kukartsev VV, Gozbenko VE, Konyukhov VY, Oparina TA. **Technogenic Reservoir Resources of Mine Methane When Implementing the Circular Waste Management Concept.** *Resources* 2024; **13**: 33.

[3] Pimentel GC, McClellan AL. **Hydrogen Bonding.** *Annual Review of Physical Chemistry* 1971; **22**: 197–222.

[4] Samuel. **Experimental and Modeling High-Pressure Study of Ammonia Oxidation.** *Energy and Fuels* 2023; **37**: 11234–11248.

[5] Degtyareva K, Tynchenko V, Kukartsev V, Khramkov V. **Use of Computer Simulation Tools to Simulate Processes at the Foundry.** *Proceedings of the 23rd International Symposium INFOTEH-JAHORINA* 2024; 199053.

[6] Kobayashi H, Hayakawa A, Kunkuma KD, Somarathne A, Okafor EC. **Science and Technology of Ammonia Combustion.** *Proceedings of the Combustion Institute* 2019; **37**: 109–133.

[7] Kukartsev V, Kravtsov K, Stefanenko O, Podanyov N, Bezvorotnykh A. **Using Machine Learning Techniques to Simulate Network Intrusion Detection.** *Proceedings of the International Conference on Intelligent Systems for Cybersecurity* 2024; 1–6.

[8] Lamb KE, Dolan MD, Kennedy DF. **Ammonia for Hydrogen Storage: A Review of Catalytic Ammonia Decomposition and Hydrogen Separation and Purification.** *International Journal of Hydrogen Energy* 2019; **44**: 12345–12360.

[9] Filina OA, Martyushev NV, Malozyomov BV, Tynchenko VS, Kukartsev VA, Bashmur KA, Pavlov PP, Panfilova TA. **Increasing the Efficiency of Diagnostics in the Brush-Commutator Assembly of a Direct Current Electric Motor.** *Energies* 2024; **17**: 17.

[10] Panfilova TA, Kukartsev VA, Tynchenko VS, Mikhalev AS, Wu X. **Treatment of Wastewater from Mining Industrial Enterprises from Phenols.** *Mining Informational and Analytical Bulletin* 2024; **7-1**: 72–82.

[11] Hayakawa A. **Detailed Kinetic Mechanism for Oxidation of Ammonia Including Nitrogen Oxide Pathways.** *Energy and Fuels* 2018; **32**: 123–134.

[12] Tynchenko YA, Kukartsev VV, Bashmur KA, Wu X, Sevryugina NS. **Probabilistic Analysis of Pump Reliability Indicators Using a Neural Network.** *Mining Informational and Analytical Bulletin* 2024; **7-1**: 126–136.

[13] Dehue M, Stagni A, Arunthanayothin S, et al. **Low- and Intermediate-Temperature Ammonia/Hydrogen Oxidation in a Flow Reactor: Experiments and Wider-Angle Kinetic Modeling.** *Chemical Engineering Journal* 2023; **471**(31): 144577.

[14] He X, Shu B, Nascimento D, Fernandes RX. **Autoignition Kinetics of Ammonia and Ammonia/Hydrogen Mixtures at Intermediate Temperatures and High Pressures.** *Combustion and Flame* 2019.

[15] Voitovich EV, Kononenko RV, Konyukhov VY, Tynchenko V, Kukartsev VA, Tynchenko YA. **Designing the Optimal Configuration of a Small Power System for Autonomous Power Supply of Weather Station Equipment.** *Energies* 2023; **16**: 5046.

[16] D'Alessio F, Lapenna PE, Creta F. **Intrinsic Instability of Lean Hydrogen/Ammonia Premixed Flames: Influence of Soret Effect and Pressure.** *ArXiv* 2023.

[17] Kondratiev VV, Klyuev RV, Karlina AI. **Improvement of Hybrid Electrode Material Synthesis for Energy Accumulators Based on Carbon Nanotubes and Porous Structures.** *Micromachines* 2023; **14**: 1288.

[18] Nizhegorodov AI, Lapshin VL, Nemchinova NV, Ilizarov DL. **Industrial Electric Furnace with Movable

Hearths for Burning Concentrates and Conglomerates of Vermiculite Ores. *Sustainable Development of Mountain Territories* 2025; **17**(1): 535–545.

[19] Klyuev RV. **Development of a Methodology for Calculating Swings in an Electrical System.** *Sustainable Development of Mountain Territories* 2024; **16**(3): 1205–1213.

[20] Tattimbek G, Sherov KT, Absadykov BN, Sikhimbayev MR. **Study the Method of Thermal Frictional Treatment of Tooth Gaps for Large-Modular Cylindrical Gears.** *Sustainable Development of Mountain Territories* 2025; **17**(1): 350–361.

[21] Bukhtoyarov VV, Wu X, Tynchenko YA, Kukartsev VA. **Overview of Methods for Enhanced Oil Recovery from Conventional and Unconventional Reservoirs.** *Energies* 2023; **16**: 4907.