

Review

Insights into the Reaction Kinetics of Hydrazine-Based Fuels: A Comprehensive Review of Theoretical and Experimental Methods

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Abstract: While researchers have extensively studied the initial decomposition mechanism of Monomethylhydrazine (MMH, CH_3NHNH_2) in the MMH/dinitrogen tetroxide (NTO) system, the investigation of Unsymmetrical Dimethylhydrazine (UDMH, $(\text{CH}_3)_2\text{NNH}_2$) has been limited due to its high toxicity, corrosiveness, and deterioration rate. Hence, the effects of UDMH's deterioration products on combustion performance and gas-phase combustion reaction mechanisms remain unclear. This comprehensive review examines the existing research on the reaction kinetics of the three widely used hydrazine-based self-ignition propellants: Hydrazine (HZ, N_2H_4); MMH; and UDMH, emphasizing the necessity for further investigation into the reaction kinetics and mechanisms of UDMH. It also discusses the implications of these findings for developing safer and more efficient rocket propulsion systems. Additionally, this review underscores the importance of utilizing computational chemistry theory to analyze hydrazine-based fuels' combustion and decomposition properties, constructing detailed pyrolysis and combustion reaction mechanisms to optimize rocket engine fuel performance and environmental concerns.

Keywords: hydrazine-based fuels; rate constants; thermochemistry; reaction kinetics; kinetic model development; experimental studies



Citation: Wu, J.; Bruce, F.N.O.; Bai, X.; Ren, X.; Li, Y. Insights into the Reaction Kinetics of Hydrazine-Based Fuels: A Comprehensive Review of Theoretical and Experimental Methods. *Energies* **2023**, *16*, 6006. <https://doi.org/10.3390/en16166006>

Academic Editor: Theodoros Zannis

Received: 3 July 2023

Revised: 3 August 2023

Accepted: 9 August 2023

Published: 16 August 2023



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1. Introduction

Hydrazine-based fuels consist of Hydrazine (N_2H_4) [1], Monomethylhydrazine (CH_3NHNH_2), and Unsymmetrical Dimethylhydrazine ($(\text{CH}_3)_2\text{NNH}_2$) [1,2]. They are strong reducing agents that remain in a liquid state at room temperature and are used in rocket propulsion systems due to their desirable characteristics: high energy density; stability; reliable ignition; high thrust-weight ratio; reactivity; efficiency; specific impulse; and storage stability at room temperature.

Hydrazine propellants offer two primary combustion modes. In the first mode, a single-component hydrazine propellant decomposes exothermically upon exposure to a catalyst or a hot surface, leading to spontaneous ignition, combustion, or explosion [3–5]. This mode generates a stable flame, enabling thrust and gas power [6]. The second mode involves mixing hydrazine with a strong oxidizer, such as inhibited red-fuming nitric acid (IRFNA) [7,8] or dinitrogen tetroxide (N_2O_4 , NTO) [9], to create a two-component propellant. Combustion of these propellants occurs in the gas phase of rocket motors for high orbital transfer and attitude control [6,10,11].

However, the combustion of hydrazine fuels and oxidizers, such as NO_2 or N_2O_4 , poses challenges, particularly at or below room temperature [12], due to their high reactivity and combustibility. For instance, mixing highly dilute gas-phase Hydrazine with NTO

can result in spontaneous ignition without ignition devices such as sparks or shock waves. This characteristic makes these fuels highly reliable in low-temperature and low-pressure environments [12]. However, determining the precise ignition mixture concentration and understanding the complete ignition process for engine design remains unclear, posing difficulties in empirically predicting their combustion and decomposition characteristics.

Researchers have focused on exploring alternative fuels with reduced toxicity to advance the development of safer and more efficient rocket propulsion systems. One avenue of research involves the utilization of ionic liquids designed with specific cations and anions to control sensitivity and thermal properties [13]. Synthesized hypergolic ionic liquids, utilizing compounds such as dicyanamide anion or 1,2,3-triazole, exhibit favorable characteristics, including high density, increased energy storage capacity, superior performance, and hydrophobic stability [13]. There is also a proposal to use various bio-based fuel alternatives as a more sustainable option [14,15].

Developing less toxic organic fuels requires a better understanding of hypergolic combustion mechanisms. Visible and near-infrared Raman spectroscopy and drop and mixing tests evaluate the reaction process and kinetics and the effect of enhanced mixing processes reducing ignition delay times. Techniques that allow estimating the production of free radicals can also give information about the chemical mechanisms [16]. A comprehensive analysis of different additives, combustion chamber geometries, ignition systems, combustion instability, flame structure, thermal decomposition products, thermal management requirements, and nozzle designs are necessary to optimize rocket engine fuel performance. Figure 1 highlights the various thermal decomposition mechanisms of hydrazine-based fuels.

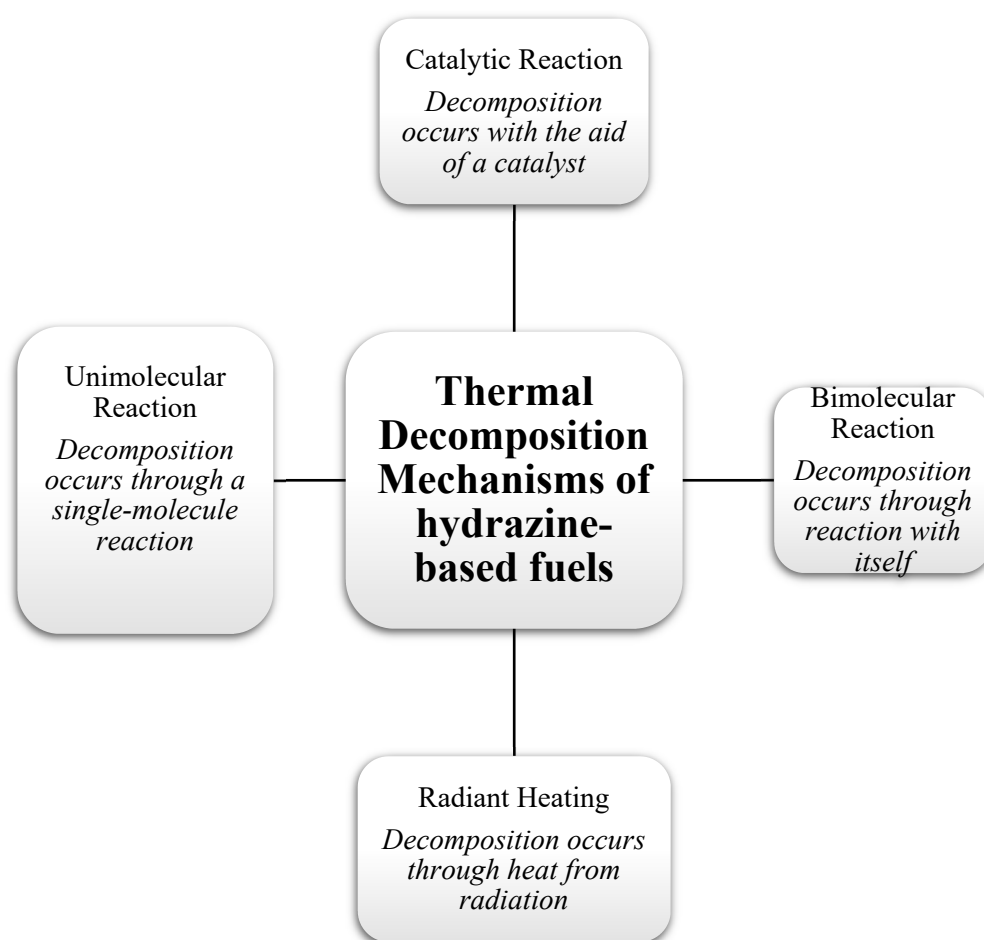


Figure 1. Thermal Decomposition Mechanisms of hydrazine-based fuels.

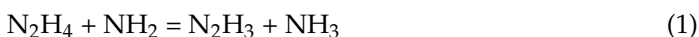
Deepening our understanding of the reaction kinetics and mechanisms of hydrazine-based fuels is crucial for advancing the development of safer and more efficient rocket propulsion systems. Theoretical approaches, such as high-precision quantum mechanical (QM) calculations and reactive molecular dynamics (MD) simulations, enable the microscopic observation of molecular and intermolecular reactions, prediction of reaction transition states and intermediates, and determination of reaction rates and thermodynamic parameters [17]. Additionally, large-scale molecular dynamics simulations aid in simulating physicochemical reactions at the molecular scale, allowing researchers to explore different reaction conditions, obtain reaction rates and core reaction paths, and construct comprehensive reaction networks. Combining these computational methods with experimental studies provides essential insights into hydrazine fuel thermochemical properties, reaction pathways, and basic mechanisms.

Furthermore, optimizing rocket engine fuel performance and addressing environmental concerns arising from the combustion of hydrazine fuels necessitates the development of detailed pyrolysis and combustion reaction mechanisms. Computational fluid dynamics (CFD) has gained equal importance to experimental methods in understanding the internal combustion processes of rocket engines. These models are essential for understanding combustion processes in the combustion chamber of rocket engines and optimizing propulsion system designs [18].

This review aims to comprehensively analyze the theoretical and experimental studies on the reaction kinetics of hydrazine-based fuels [19]. It explores the available research on thermochemical properties and various reactions, reaction kinetics, and mechanisms of hydrazine-based fuels. It further emphasizes the implications of these findings for developing safer and more efficient rocket propulsion systems.

2. Research Status on Anhydrous Hydrazine Fuel

Understanding anhydrous hydrazine fuel combustion kinetics is crucial in various engineering and scientific applications. Combustion kinetic studies of hydrazine, often based on incomplete kinetic mechanisms [20–23], started with rate constants [24–31] estimation for the reactions of N_2H_4 with atoms or radicals [25,30–35]. In 1953, Avery et al. [24] constructed a model for hydrazine decomposition in an excitation tube. They later adjusted [36] this model, and the simulation results were consistent with the overall decomposition rate of N_2H_4 measured experimentally [25]. In 1998, Konnov et al. [36] adjusted the reaction rate constant for the reaction stated in Equation (1) based on the decomposition of N_2H_4 and flame experimental data.



They updated a primary mechanism for the decomposition of N_2H_4 based on a complete set of N/H reactions [36], mainly by correcting the thermodynamic data of N_2H_x substances and the reaction rate constants [37] of several reactions closely related to the decomposition of N_2H_4 . The updated hydrazine decomposition model at high temperatures [38] contained 51 reactions and 11 substances. Catoire et al. [39] also developed a detailed N_2H_4 decomposition chemical kinetic mechanism, consisting of 13 chemicals and 33 essential reactions, to simulate the explosion of pure N_2H_4 vapor. Sawyer and Glassman et al. [40] studied the gas-phase reactions of N_2H_4 with O_2 , NO , and NO_2 . They showed that the high activity reactions of N_2H_4 and NO_2 were caused by the continuous abstraction of H atoms on N_2H_4 by NO_2 .

2.1. Hydrazine Combinations with Other Species

Izato et al. [41] presented a chemical mechanism for the early stage of hypergolic ignition in liquid hydrazine/nitrogen tetroxide mixtures commonly used as propellants in spacecraft. The mechanism determined through quantum chemical calculations showed that the energy barrier to the reaction between N_2H_4 and N_2O_4 was much lower than predicted for the same reaction in the gas phase. The study provides insights into the

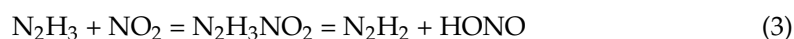
detonation-like ignition of these propellants. However, further experimental data are needed to validate the hypothesis presented in their study.

Wasko et al. [42] and Chuan et al. [43] investigated the gas-phase reaction of $\text{N}_2\text{H}_4/\text{NO}_2$ - N_2O_4 experimentally by introducing N_2H_4 and NTO liquid propellant into a vacuum chamber, which created spontaneous combustion at temperatures below 300 K. Tanaka et al. [44] observed the combustion of N_2H_4 droplets at room temperature using a high-speed camera. The N_2O_4 droplets were dropped into the N_2H_4 liquid pool. Less than 5 μs after contact and before the onset of ignition, the surface layers of both liquids began to evaporate in an explosion-like reaction. The N_2O_4 vapor penetrated the N_2H_4 pool before ignition. For the same mass, the N_2H_4 /NTO two-component fuel had an explosive power equivalent to 160% of Trinitrotoluene (TNT) [45]. Miyajima and Sakamoto [46] measured the ignition delay time at 40–90 torr, from 343 to 433 K, in a diffusion flame experiment with N_2H_4 /NTO.

Daimon et al. [45,47] investigated the nature and mechanism of contact explosions of spontaneous liquid propellants with combinations of fuels and oxidizers. The results show that the observed explosion phenomena can be classified into two categories. First, sudden, spontaneous vaporization of the superheated N_2H_4 /NTO liquid layer formed at the boundary between the two liquids occurs. A burst-like reaction takes place in the resulting reaction mixture. Chemical reactions did not enhance the abrupt vaporization with weak explosions. Second, the shock of local ignition causes the sudden vaporization of MMH/NTO and UDMH/NTO, and a turbulence-combustion reaction occurs in the resulting reaction mixture.

Ohminami et al. [48] developed the gas-phase chemical reaction mechanism [49] for N_2H_4 /NTO, containing 64 species and 22 chemical reactions. The hydrazine decomposition reaction rate was improved and validated by experimental results from the literature [48]. The model influenced fuel film cooling behavior simulation and improved the combustion chamber wall temperature prediction. The model had good prediction capability for hydrazine and NTO reactions. CFD simulation results show that the nitric oxide reaction affects the ignition delay time and initiates combustion. However, low temperature is insufficient to cause the decomposition reaction of the substances, and the mechanism cannot explain the spontaneous combustion of the system at low temperatures. These studies on two systems highlight the importance of understanding the mass transfer characteristics of hydrazine in mixture systems and other species' effects on hydrazine's combustion and kinetics.

Daimon et al. [50] evaluated the thermochemical data of chemical species [17] associated with the combustion of $\text{N}_2\text{H}_4/\text{NO}_2$ with quantum chemical calculations at the CBS-QB3 level of theory and constructed a primary chemical kinetic mechanism for the gas-phase combustion of $\text{N}_2\text{H}_4/\text{NO}_2$ mixtures. Kinetic simulations showed that the sequential reactions [51], as shown in Equations (2)–(5), cause low-temperature spontaneous combustion fires.



The rate constants of these reactions were also estimated based on transition state theory and single molecule rate theory. The proposed mechanism can predict the low-temperature ignition of $\text{N}_2\text{H}_4/\text{NO}_2$ mixtures. These reactions release much heat, especially in Equation (5) which produces N_2 . The temperature increase accelerates Equation (2) with a small activation potential. After that, Daimon et al. [52] extensively explored the extensive

reaction pathways between N_2H_4 and NO_2 through quantum chemical calculations and developed a kinetic reaction mechanism for the spontaneous ignition of $\text{N}_2\text{H}_4/\text{NO}_2$ gas mixtures. As shown in Equation (6), the mechanism shows that ignition proceeds mainly through this reaction, explaining the spontaneous ignition of the $\text{N}_2\text{H}_4/\text{NTO}$ system at temperatures below -173°C .



where $m = 1$ to 4.

Lai et al. [53] studied the reaction of N_2H_4 with N_2O_4 isomers at the level of G2M(CC3)//B3LYP/6311++G(3df, 2p). The results show that the reactions of N_2H_4 with sym- N_2O_4 (D2h), cis-ONONONO₂ (Cs), and NO_2 need to overcome energy barriers of 14.2, 10.6, and 7.6 kcal/mol, respectively [51]. In contrast, N_2H_4 can react spontaneously with trans-ONONONO₂ (Cs) and cis-ONONONO₂ (C_1) to form $\text{HONO}_2 + \text{H}_2\text{NN}(\text{H})\text{NO}$ with an approximate kinetic gas rate constant above 250 K of $4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The resulting $\text{H}_2\text{NN}(\text{H})\text{NO}$ can be rapidly cleaved to generate reactive N_2H_3 radicals with a rate constant greater than $1 \times 10^7 \text{ s}^{-1}$ above 1000 K, sufficient to initiate spontaneous combustion chain reactions with NO_2 and N_2O_4 [51].

Huyen et al. [54] further investigated the kinetics and mechanism of the spontaneous combustion reactions of N_2O_4 with N_2H_4 and CH_3NHNH_2 using ab initio molecular orbital theory based on the UCCSD(T) method with 6-311+G(3df, 2p) as the basis set. They illustrated that the spontaneous ignition reactions of N_2O_4 with N_2H_4 and CH_3NHNH_2 to produce $\text{N}_2\text{H}_3\text{NO} + \text{HNO}_3$ and $\text{CH}_3\text{NHN}(\text{H})\text{NO}/\text{CH}_3\text{N}(\text{NO})\text{NH}_2 + \text{HNO}_3$, respectively, are triggered by the rapid attack of ONONO₂ on the hydrazine molecule. NTO is isomerized at an energy barrier higher than that of the reactants by 5.9 kcal/mol and 6.3 kcal/mol. The authors highlight [54] the short half-life of N_2O_4 in a mixture containing excess N_2H_4 at atmospheric, reflecting the effective self-ignition initiation of these propellant systems [54]. Using the transition state theory in the temperature range from 298 to 2000 K, the rate constant of the formation of $\text{N}_2\text{H}_3\text{NO}$ and HNO_3 was estimated, as shown in Figure 2, as well as the rate constant of the bimolecular reaction of N_2O_4 with CH_3NHNH_2 , as shown in Figure 2.

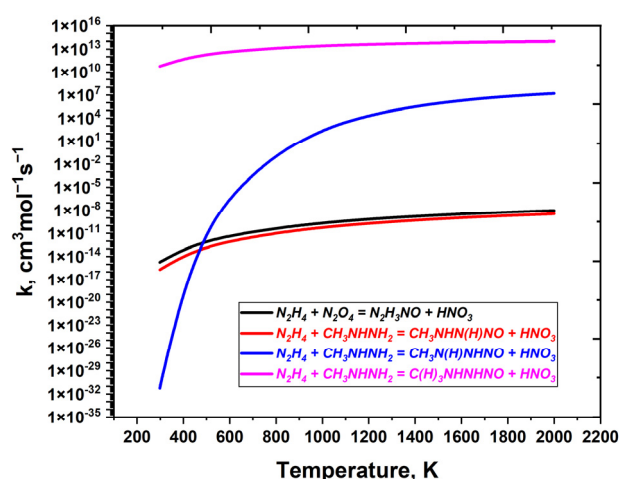


Figure 2. Ignition Reactions of N_2H_4 with N_2O_4 and CH_3NHNH_2 .

Table 1 highlights the Arrhenius fit parameters calculated in various studies relating to hydrazine.

Table 1. Some Reactions Involving Hydrazine.

Reaction	A (s^{-1} or $cm^3 mol^{-1} s^{-1}$)	n	Ea (cal/mol)	References
$NH_2 + NH_2 = N_2H_4$	3.12×10^{13}	0	0	[55]
$NH_2 + NH_2 = N_2H_4$	5.14×10^{10}	0	0	[56]
$N_2H_4 (+M) = NH_2 + NH_2 (+M)$	5.00×10^{14}	0	251.21	[38]
$NH_2 + NH_2 = NH_3 + NH$	3.37×10^7	2.82	2.22×10^3	[55]
$NH_2 + NH_2 = NH_3 + NH$	5.00×10^{13}	0	9.94×10^3	[39]
$N_2H_4 + H = N_2H_3 + H_2$	9.60×10^8	1.5	4.83834×10^3	[39,56]
$N_2H_4 + H = N_2H_3 + H_2$	7.00×10^{12}	0	10.47	[38]
$N_2H_4 + NH_2 = N_2H_3 + NH_3$	3.70×10^6	1.94	1.62934×10^3	[39,56]
$N_2H_4 + NH_2 = N_2H_3 + NH_3$	1.80×10^6	1.71	−5.78	[38]

The formation of NH_3 from NH_2 , the H-atom abstraction reaction [57] of N_2H_4 with H, and the H-atom abstraction reaction of N_2H_4 with NH_2 , are shown in Figures 3–5, respectively. A comparison of each reaction's rate constant generally shows a difference in rate constants by several magnitudes of order for the same reaction. This disparity is due to the different approaches used in the literature for calculating and estimating these rate constants in different mechanisms.

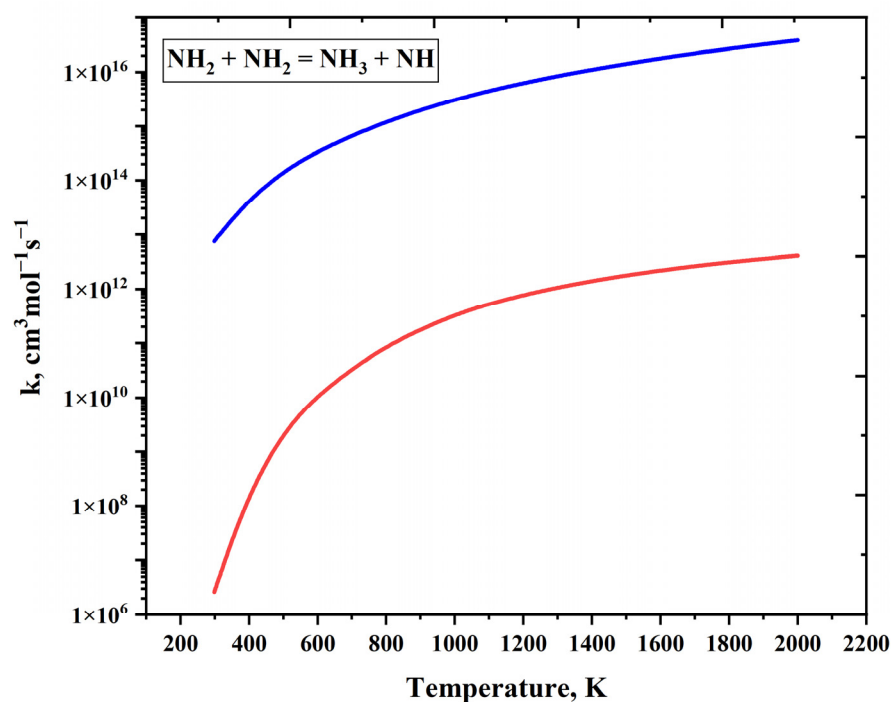


Figure 3. Formation of NH_3 from NH_2 . (Blue line from Asatryan et al., 2010 [55]; Red line from Catoire et al., 2001 [39]).

Table 2 summarizes some research on hydrazine and its combination with other fuels' combustion.

2.2. Critical Assessment of the Research on Hydrazine

While the reviewed studies on anhydrous hydrazine fuel combustion kinetics have provided valuable insights, it is essential to acknowledge the limitations and identify areas that require further investigation.

The combustion studies relied on incomplete kinetic mechanisms for hydrazine fuel. These mechanisms may not accurately capture all relevant reactions and pathways involved in combustion. Further research is needed to develop comprehensive and accurate kinetic mechanisms that provide a detailed understanding of hydrazine fuel combustion behavior.

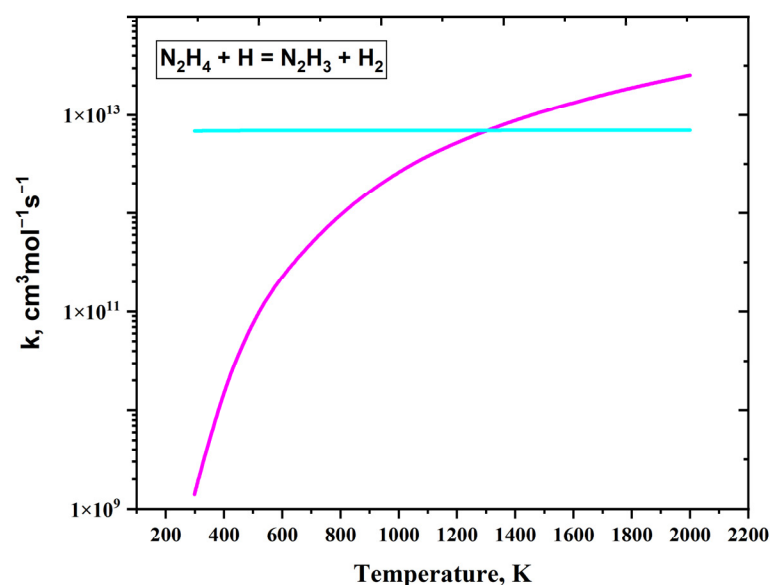


Figure 4. H-atom abstraction reaction of N_2H_4 with H. (Magenta line from Dean and Bozzelli, 2000 [56]; Cyan line from Catoire et al., 2001 [39]).

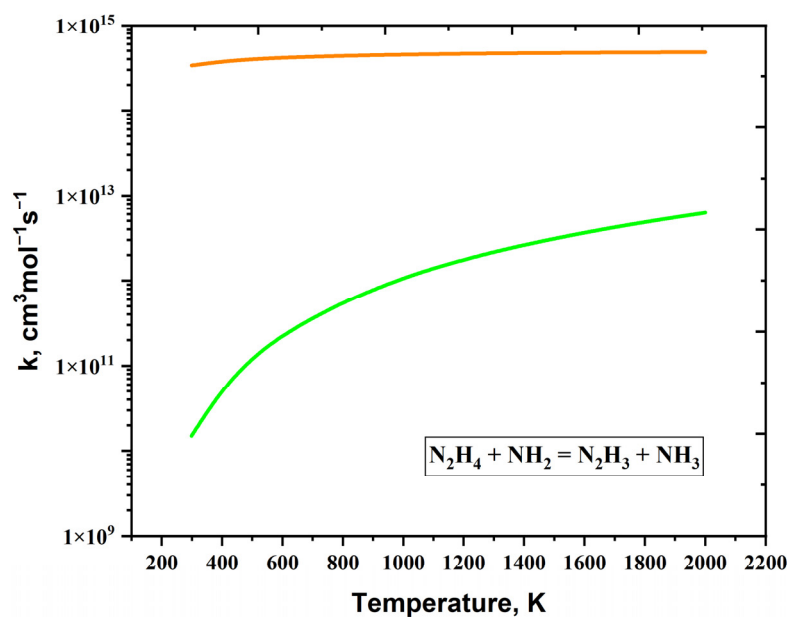


Figure 5. H-atom abstraction reaction of N_2H_4 with NH_2 . (Green line from Konnov et al. [38], 2001; Orange line from Catoire et al., 2001 [39]).

Despite the significant body of research, comprehensive and well-documented experimental data still lacks. More systematic and extensive experimental investigations are needed to validate and expand existing knowledge. Additionally, more data are required at low temperatures, as current mechanisms struggle to explain spontaneous combustion at low temperatures.

Studies have primarily focused on fundamental reactions and kinetics. However, further exploration and understanding of complex phenomena, such as film-cooled drying mechanisms and fuel-oxidizer mixture flame construction, are needed. These phenomena significantly impact engine performance and safety.

While detailed kinetic models have been developed, there is a need for more comprehensive modeling approaches. These models should accurately capture interactions between species and reactions, considering temperature, pressure, and other environmen-

tal factors. Advanced and validated models will enable more accurate predictions and simulations of hydrazine fuel combustion.

Table 2. Details of Hydrazine and combination with other fuels research.

Researchers	Details
Avery et al. [24]	Constructed a model for hydrazine decomposition
Just [58]	Conducted a series of studies on the N ₂ H ₄ /NTO combination fuel
Sawyer and Glassman et al. [40]	Studied the gas-phase reactions of N ₂ H ₄ with O ₂ , NO, and NO ₂
Konnov et al. [36]	Adjusted the reaction rate constant for the reaction N ₂ H ₄ + NH ₂ → N ₂ H ₃ + NH ₃ based on the decomposition of N ₂ H ₄ and flame experimental data
Konnov et al. [38]	Developed a kinetic reaction mechanism for the decomposition of hydrazine at high temperatures, containing 51 reactions and 11 substances
Ohminami et al. [48]	Developed a gas-phase chemical reaction mechanism of N ₂ H ₄ /NTO, containing 64 and 22 chemical reactions, and performed a series of CFD simulations
Daimon et al. [50]	Investigated the nature and mechanism of contact explosions of spontaneous liquid propellants
Izato et al. [41]	Presented a chemical mechanism for the early stage of hypergolic ignition in liquid hydrazine/nitrogen tetroxide mixtures
Golden et al. [59]	Studied the decomposition of hydrazine fuels at pressures of 0.1–10 mTorr by the ultra-low-pressure pyrolysis technique (VLPP). They measured the reaction rate constants for the decomposition of Hydrazine single molecules due to collisions

Theoretical calculations and modeling techniques were heavily relied upon. Experimental validation and verification of these findings are necessary. More experimental studies are required to validate proposed mechanisms and reaction rates, providing robust and reliable data for future research and application. Figure 6 further summarizes the identified limitations.

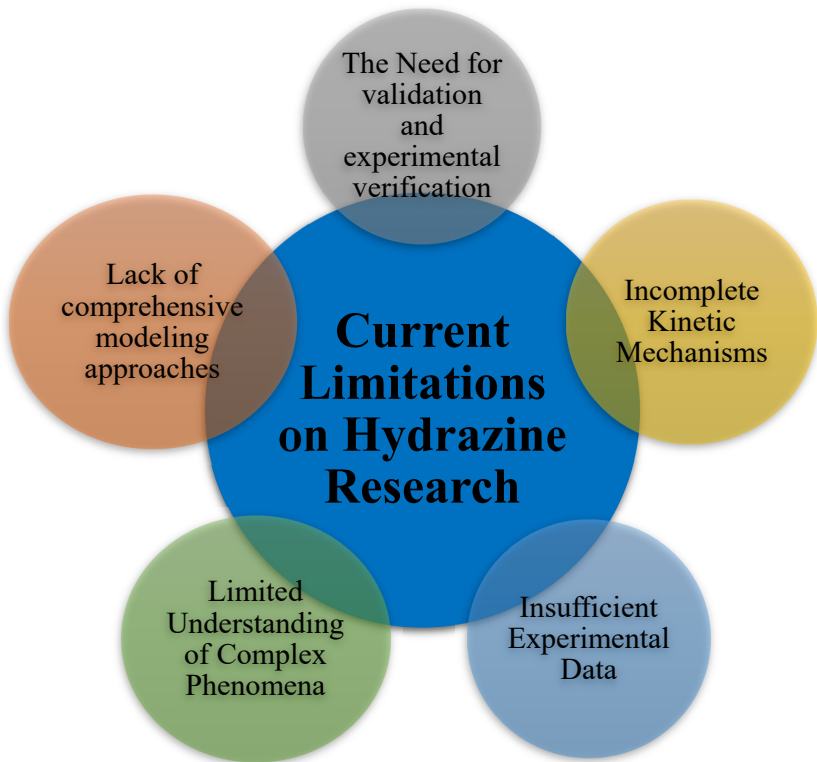


Figure 6. Current Limitations on Hydrazine Research.

2.3. Research Status on MMH Fuel

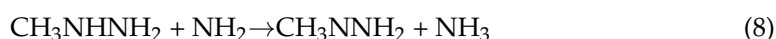
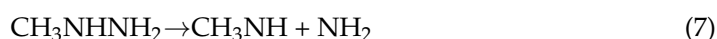
MMH is an essential compound in engineering and science due to its potential applications in propulsion systems and other industrial processes. Understanding MMH's decomposition kinetics, reaction mechanisms, and combustion properties is crucial for optimizing performance, ensuring safety, and improving efficiency in these applications. Methylhydrazine (CH_3NHNH_2 , MMH) is formed when a methyl group replaces an H atom on N_2H_4 . In the 1960s, Kerr et al. [33] investigated the primary reaction rate constants for uniform bond breaking of N-N bonds in N_2H_4 and MMH [60]. Eberstein and Glassman [25] studied N_2H_4 , MMH, and UDMH decomposition reactions at atmospheric pressure and 750–1000 K in adiabatic conditions. The decreasing order of magnitude of the decomposition rate was $\text{UDMH} > \text{MMH} > \text{N}_2\text{H}_4$.

Catoire et al. [61] conducted a pyrolysis study of 1–3% MMH/argon mixtures in 38.4 mm excitation tubes in the temperature range of 1040 to 1370 K and pressure range of 1.4 to 4.5 atm. A simplified kinetic model and mechanistic diagram were also presented to interpret the experimental data. The results show that MMH can decompose exothermally at 70 to 80 mol% argon dilution. The complete kinetic model can simulate this explosive decomposition reaction, showing that pure gaseous MMH is much less sensitive to explosive bombardment than hydrazine.

For the theoretical calculation of the pyrolysis reaction kinetics of MMH, Sun and Law [62] investigated the kinetics of the thermal decomposition reaction of MMH using the quantum Rice–Ramsperger–Kassel (QRRK) theory and pressure drop master equation analysis. The potential barrier was calculated at the B3LYP/6-311G(d,p) level, and the enthalpies of production, ΔH°_f (298.15 K) of the parent MMH (CH_3NHNH_2) and its corresponding radicals CH_3NNH_2 , CH_3NHNH , and CH_2NHNH_2 were determined to be 21.6, 48.5, 51.1, and 62.8 kcal/mol, respectively, by isocratic reaction analysis and various ab-initio calculation methods. The kinetic analysis undertaken at the CBS-QB3 level and simulating MMH's homogeneous decomposition under atmospheric pressure conditions informed that the N-N and C-N bond-breaking reactions are the main pathways.

Subsequently, Sun et al. [63] further updated the mechanism with experimental data on MMH excitation tube pyrolysis at 900–1370 K, 1.4–4.5 atm. They used the model to predict the decomposition curves and half-life decomposition times of seven sets of MMH/Ar mixtures at different temperatures and pressures for the excitation tube experiments. Good agreement was observed for dilute MMH/Ar mixtures below 940 K and above 1150 K. Model predictions further indicated that the overall MMH decomposition rate is consistent with first-order kinetics and that N-N bond splitting is the most sensitive reaction pathway to simulate homogeneous decomposition of MMH at high pressures. The model predicts longer ignition delays for high-concentration MMH/Ar mixtures. However, predictions deviate from experimental data with a latency of about 100 μs in the temperature range of 1030 to 1090 K.

Cook et al. [64] made the first measurements of the time histories of NH_2 and NH_3 during MMH pyrolysis after reflecting excitation waves in an excitation tube using an improved method of laser absorption techniques, with MMH at a concentration of ~1% in Ar, in the 941 to 1252 K temperature range, and pressures close to 2 atm. NH_3 and MMH were measured by direct absorption with CO_2 laser lines at 9.22 and 10.22 μm , respectively. Based on NH_2 and NH_3 , two critical reactions in the MMH pyrolysis system can be measured, as shown in Equations (7) and (8).



The rate coefficients of the MMH pyrolysis system combined with the measured total MMH decomposition rates indicate that reaction (7) is the main MMH decomposition channel. The rate coefficients (2 atm, 900–1300 K) are $k_1 = 1.50 \times 10^{58} \times T^{-12.84} \exp(-39,580/T) \text{ s}^{-1}$,

$k_2 = 3.70 \times 10^{14} \exp(-2620/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The changes made to the MMH pyrolysis mechanism significantly improved the measured and simulated NH_2 , NH_3 , and MMH time histories over the entire range of study.

Li et al. [60] studied the pyrolysis of MMH in a surge tube and measured the time histories of NH_2 concentrations in MMH/argon mixtures in the temperature range from 1100 to 1400 K, with pressures from 0.3 to 5 atm and showed that the above k_1 has a pressure dependence at 0.3 to 5 atm and the measured reaction rate constants follow a pressure-dependent trend.

Zhang et al. [65] pointed out that simple N-N and C-N bond fission to generate radicals $\text{CH}_3\text{NH} + \text{NH}_2$ or $\text{CH}_3 + \text{NHNH}_2$ dominates the decomposition kinetics. The pressure dependence and product branching during the dissociation of CH_3NHNH_2 were predicted by solving the master equation. This study analyzed the kinetics of $\text{NH}_2 + \text{CH}_3\text{NH}$ and $\text{CH}_3 + \text{NHNH}_2$ unblocked binding reactions and the corresponding MMH dissociation reaction kinetics associated with rocket motor combustion over a wide range of temperatures and pressures, yielding $\text{NH}_2 + \text{CH}_3\text{NH}$ channels as the dominant channels.

Sun et al. [66] identified various MMH decomposition pathways using QCISD(T)/cc-pV ∞ Z//CASPT2/aug-cc-pVTZ or QCISD(T)/cc-pV ∞ Z//B3LYP/6-311++G(d,p) quantum chemical methods. The results show that CH_2NNH_2 has an energy barrier of 13.8 kcal mol $^{-1}$, and β -cleavage to methyleneimine is the main pathway for the decomposition of CH_2NNH_2 radicals. The high-pressure limiting rate coefficient of the reaction is $3.88 \times 10^{19} T^{-1.672} \exp(-9665.13/T) \text{ s}^{-1}$. In addition, the pressure-dependent rate coefficient exhibits a slight temperature dependence in the temperature range from 1000 to 2500 K. They also calculated the reaction's dissociation and isomerization rate coefficients by E/J-resolution RRKM theory and porous master equation analysis at 300 to 2500 K and 0.01 to 100 atm pressures. The calculated rate coefficients associated with the latest thermochemical property data are essential in developing the kinetic mechanism of pyrolysis and oxidation of MMH and its derivatives.

NO_2 is one of the main components of NTO, which continuously abstracts H atoms on MMH intermediate N at low temperatures to produce products (CH_3NNH_2 and HONO), after which HONO cleaves exothermally to produce $\dot{\text{O}}\text{H}$ radicals, which is the main reaction that induces ignition. McQuaid and Ishikawa [67] characterized the path static point of NO_2 extraction of H atoms from MMH by CCSD(T)/6-311++G(3df,2p)//MPWB1K/6-31+G(d,p) and CCSD(T)/6-311+G(2df,p)//CCSD/6-31+G(d,p) calculations. Five transition states connecting the $\text{CH}_3\text{NHNH-NO}_2$ complexes, including $\text{CH}_3\text{NHNH-HONO}$, $\text{CH}_3\text{NNH}_2\text{-HONO}$, $\text{CH}_3\text{NNH}_2\text{-HNO}_2$, and $\text{CH}_3\text{NHNH-HNO}_2$ complexes, were determined. The highest point of the minimum energy path from the $\text{CH}_3\text{NHNH}_2 + \text{NO}_2$ reaction asymptote to the HONO-containing product is 8.6 kcal/mol of the transition state. This value is considerably higher than the 5.9 kcal/mol estimated from the theoretical results of extracting H atoms from NH_3 by NO_2 .

Kanno et al. [68] further investigated the reaction kinetics and mechanism of H-atom extraction from MMH by NO_2 theoretically. The dissociation and isomerization steps between the intermediate complexes were necessary for distributing the dissociated bimolecular products. At lower temperatures, the major products are cis- CH_3NHNH and HONO. The branching rate of the CH_3NNH_2 formation pathway increases with increasing temperature. On the same reaction potential energy surface, six reactions, such as the isomerization reaction of CH_3NNH_2 catalyzed by HONO with cis/trans- CH_3NHNH , are proposed as competing reactions. Temperature- and pressure-based kinetic model rate expressions were proposed.

Liu et al. [69] used Fourier transform infrared spectroscopy (FTIR) to experimentally study the gas-phase chemistry of the spontaneous combustion system of MMH with oxidant $\text{NO}_2/\text{N}_2\text{O}_4$ at room temperature and 1 atm N_2 and performed quantum mechanical calculations (CCSD(T)/M06-2X) of possible reaction pathways. Based on these studies, they proposed that the oxidation of MMH in the NO_2 atmosphere occurs through two mechanisms: sequential extraction of H and generation of HONO; and the reaction of MMH

with asymmetric ONONO₂ to generate methyl nitrate. These mechanisms successfully explain all the intermediates observed experimentally.

In addition to the H-atom abstraction of MMH by NO₂, OH reactive radicals are an essential component of the pyrolysis reaction. Harris et al. [70] and Vaghjiani [71] experimentally measured the total reaction rate of H-atom removal from MMH by OH, where Vaghjiani et al. [71] obtained the absolute second-order OH rate coefficient expression in the temperature range of 232 to 637 K as $k_2 = (4.59 \pm 0.83) \times 10^{-11} \exp(85 \pm 35)/T \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The hydroxide (OH) radical H-atom abstraction reaction showed no identifiable pressure dependence at He or N₂ buffer gas pressure up to 530 torrs.

Liu et al. [72] performed a direct kinetic study of the multichannel reaction of MMH with OH radicals and identified five hydrogen extraction channels. Electronic structure information on the potential energy surface was obtained at the B3LYP/6-311G(d,p) level. The energies on the reaction path were refined by the BMC-CCSD method. The results show that H-atom abstraction from -NH- is the main pathway for Conformer I at low temperatures; with increasing temperature, H-atom abstraction from -NH₂ is a competing pathway. For Conformer II, a similar conclusion can be drawn. Starting from the Boltzmann distribution function and considering the weight factor of each conformation to calculate the total rate constant, the three Arrhenius expressions between 200 and 1000 K were fitted as $k_T = 1.63 \times 10 T^{-244.03} \exp(1411.5/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Sun et al. [73] further obtained the detailed H-atom abstraction reaction rates of MMH + OH for the four channels by theoretical calculations in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and found that the rate coefficient for the extraction of central amine H to generate CH₃NNH₂ radicals is $k_1 = 3.37 \times 10 T^{-161.295} \exp(1126.17/T)$ and an extraction of terminal amine H to generate trans-CH₃NHNH radicals rate coefficient of $k_2 = 2.34 \times 10 T^{-171.907} \exp(1052.26/T)$, a rate coefficient of terminal amine H extraction to generate cis-CH₃NHNH radicals of $k_3 = 7.41 \times 10 T^{-202.428} \exp(1343.20/T)$, and a rate coefficient of methyl H atom abstraction to generate CH₂NHNH₂ radicals of $k_4 = 9.13 \times 10 T^{-212.964} \exp(-114.09/T)$.

In addition, the radical CH₃NH generated by N-N bond breaking in MMH is unstable. It undergoes β-bond breaking to produce the stable CH₂=NH and many free H radicals. H is very reactive and reacts continuously with MMH. Vaghjiani [74] reported the total reaction rate constant for H-atom removal by H on MMH at 298 K, 26.0 Torr. Wang et al. [75] investigated the multichannel reaction mechanisms CH₃NHNH₂ + H → product (R1) and (CH₃)₂NNH₂ + H → product (R2) and studied their dynamic properties using a two-energy direct kinetic approach. The rate constants of the reactions were evaluated in the temperature range of 200 to 2000 K using a small curvature tunneling correction at the MCG3MPWPW91//MPW1K/6-311G(d,p) level, using typical variational transition state theory. Theoretical and experimental studies have shown that substituting H with CH₃ groups significantly increases the reaction rate coefficient.

Sun et al. [19] performed a detailed analysis of this class of reactions and calculated to obtain their reaction rate constants, and the results showed that the abstraction energy barriers of the central amine H atom, the two terminal amine H atoms, and the methyl H atom were 4.16, 2.95, 5.98, and 8.50 kcal mol⁻¹, respectively. The rate coefficients in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the temperature range of 290 to 2500 K were:

$$k_1 = 9.63 \times 10 T^{-202.596} \exp(-154.2/T) \quad (9)$$

$$k_2 = 2.04 \times 10 T^{-182.154} \exp(104.1/T) \quad (10)$$

$$k_3 = 1.13 \times 10 T^{-202.866} \exp(-416.3/T) \quad (11)$$

$$k_4 = 2.41 \times 10 T^{-233.650} \exp(-870.5/T) \quad (12)$$

The results indicate that the abstraction of terminal amine H atoms to form trans-CH₃NHNH radicals is the primary channel among the different abstraction channels. The theoretical H abstraction rate coefficient is $8.16 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K without adjustable parameters. Some important reaction rate constants are reported for removing H atoms from MMH by radicals ($\dot{\text{C}}\text{H}_3$, NH_2) [76].

In 1995, Illincic et al. [77] developed a set of reaction mechanisms (43 substances, 204 reactions) containing H/C/N/O for simulating the combustion of dual-based propellants (nitrocellulose and nitroglycerine). Later, Catoire et al. [78] presented the gas-phase thermochemistry of more than 50 C/H/N species and developed the MMH/O₂ [79] and MMH/NTO [80] systems for ignition and combustion. The primary reaction mechanism of the MMH/O₂ system consists of 70 species and 373 equilibrium primitive reactions with good agreement between measured and calculated values of ignition delay times in dilute and dilute mixtures. The primary reaction mechanism of the MMH/NTO system consists of 403 equilibrium reactions between 82 species, with preliminary identification of important reactions for combustion above 1000 K.

Glarborg et al. [81] developed a reaction mechanism for the decomposition of nitromethane (CH₃NO₂). Anderson et al. [82] published a reaction mechanism for MMH/FRNA containing 81 substances and 513 reactions, which is now the only more detailed and complete reaction mechanism for MMH/FRNA two-component propellants. In 2006, Catoire et al. [83] observed and analyzed the MMH/NTO self-ignition process using a constant volume bomb device and a high-speed camera and obtained critical images of combustion, which are essential for preventing two-component propellant vapor mixing. Hou et al. [84] investigated numerically with CFD simulations for a small liquid rocket engine's combined MMH/NTO propellant reaction mechanism for some practical applications. Table 3 summarizes some of the studies conducted on MMH.

Table 3. Some MMH studies and findings.

Study	Description and Findings
Kerr et al. [33]	Investigated primary reaction rate constants for uniform bond breaking of N-N bonds in N ₂ H ₄ and MMH
Eberstein and Glassman [25]	Studied decomposition reactions of N ₂ H ₄ , MMH, and UDMH in adiabatic flowers at atmospheric pressure 750–1000 K
Catoire et al. [9]	Conducted a pyrolysis study of 1–3% MMH/argon mixtures in 38.4 mm excitation tubes in the temperature range of 1040 to 1370 K and pressure range of 1.4 to 4.5 atm. MMH can decompose exothermally at 70–80 mol% argon dilution. Pure gaseous MMH is much less sensitive to explosive bombardment than hydrazine
Sun and Law [62]	Investigated the kinetics of the thermal decomposition reaction of MMH using quantum Rice–Ramsperger–Kassel (QRRK) theory and pressure drop master equation analysis. N-N and C-N bond-breaking reactions are the main reaction pathways simulating the homogeneous decomposition of MMH under atmospheric pressure conditions
Sun et al. [65]	Using laser absorption techniques, measured the time histories of NH ₂ and NH ₃ during MMH pyrolysis after reflecting excitation waves in an excitation tube. N-N bond splitting is the most sensitive reaction pathway to simulate the homogeneous decomposition of MMH at high pressures. Overall MMH decomposition rate is consistent with first-order kinetics

Critical Assessment of Existing Literature

The reviewed studies provide valuable insights into MMH's thermal decomposition kinetics, reaction mechanisms, and combustion properties. Understanding the practical

implications would help researchers and practitioners optimize MMH fuel utilization, safety protocols, and performance in specific applications. Other areas for analysis are discussed next.

Understanding MMH Decomposition at Different Pressure Ranges: While the reviewed studies have shed light on MMH decomposition at atmospheric pressure, there is a lack of research on its behavior under different pressure conditions. Further studies could explore the kinetics and mechanisms of MMH decomposition at low and high pressures, providing a comprehensive understanding of its behavior across various operating conditions.

Investigating MMH Combustion in Combination with Various Oxidizers: Most reviewed studies focused on MMH decomposition and reaction kinetics in isolation. Future research could explore the behavior of MMH in combination with different oxidizers, such as nitrogen tetroxide (NTO) or nitrous oxide (N₂O), to better understand the combustion characteristics and combustion efficiency of MMH-based propellants. This would facilitate the optimization of propellant formulations for specific applications.

Studying MMH Stability and Aging: Understanding MMH fuel's stability and aging characteristics is crucial for safe handling and storage. Further research could focus on investigating the long-term stability of MMH under various storage conditions, such as temperature, pressure, and exposure to contaminants. This would contribute to developing guidelines for the safe storage and transportation of MMH fuel.

Exploring Alternative MMH Decomposition Pathways: While the reviewed studies have provided insights into the primary decomposition pathways of MMH, there may be alternative or secondary pathways that have not been extensively explored. Further investigation could focus on identifying and characterizing these alternative pathways, which could impact the overall reaction kinetics and product formation during MMH decomposition.

Modeling and Simulation of MMH Combustion and Ignition: The development of accurate and reliable numerical models for simulating MMH combustion and ignition is essential for predicting and optimizing the performance of propulsion systems. Future research could refine existing kinetic models and reaction mechanisms to improve their predictive capabilities. Additionally, experimental data from different operating conditions can validate and calibrate these models, ensuring their accuracy and applicability.

Investigating the Environmental Impact of MMH Combustion: While the reviewed studies primarily focus on the combustion and reaction kinetics of MMH, future research could explore the environmental impact of MMH combustion. This could include the study of emissions and their effects on atmospheric chemistry. Understanding the environmental implications of MMH combustion would aid in developing cleaner and more sustainable propulsion systems.

By addressing these research gaps and pursuing these future directions, researchers can advance the understanding of MMH fuel, optimize its performance, enhance safety measures, and contribute to developing more efficient and environmentally friendly propulsion systems.

2.4. Research Status on UDMH Fuel

Unsymmetrical Dimethylhydrazine (UDMH) is widely used as the primary fuel for rocket engines in strategic missile and space fields. However, during the actual propellant storage, re-injection, and end-of-life disposal, a large amount of exhaust gas of UDMH enters the atmosphere. Based on the data for improvement kinetic reaction constants, UDMH is mainly converted to nitroso dimethylamine (NDMA) by ozone oxidation [85]. For the mechanism of UDMH oxidation to NDMH, Tuazon et al. [86] and Hong et al. [87] suggest that the pathway of NDMH generation is to generate (CH₃)₂NN(H) radicals after the hydrogen atoms are removed from UDMH. Then the radicals undergo further oxygenated dehydrogenation.

However, Liu et al. [88] and Zhang et al. [89] believe that the initiation process of UDMH is adding an oxygen atom to the NH_2 functional group. The resulting $(\text{CH}_3)_2\text{NN}(\text{O})\text{H}_2$ is further oxygenated, hydrogen transferred, and the dehydration reaction is converted into NDMA. However, the atmospheric environment is a complex system with various oxidants. The mechanism and path of UDMH conversion to NDMA under the simultaneous action of various oxidants are not precise. The oxygenation or hydrogen capture reaction in the process of UDMH oxidation to generate NDMA is dominant. Therefore, there is a need to explore multiple reaction pathways under the action of different oxidants to determine the main pathways for NDMA formation from UDMH in the atmosphere.

In addition, UDMH is the primary fuel for conventional liquid missiles. It will slowly oxidize or decompose during long-term storage to produce trace oxidation products, such as dimethylamine, meta-hydrazone, and other impurities. Currently, the interaction of UDMH with constant oxygen has been studied more. Wang et al. [90] analyzed the initial oxidation products of UDMH using the gas chromatography–mass spectrometry method. The results showed seven oxidation products in the initial stage of UDMH oxidation in the air not larger than 100 h. The concentrations of dimethylamine, meta-hydrazone, and nitroso dimethylamine increased slowly. Then, as the oxidation of UDMH continued, the concentration of dimethylamine decreased. The concentration of nitroso dimethylamine increased rapidly, and new oxidation products appeared. The mass spectra of nitrogen-containing organic compounds all contained fragment ion peaks with $m/z = 42$ to 43 , indicating that the N–N bonds of UDMH and nitrogen-containing organic oxide molecules were easily broken by heat.

Zhang et al. [91] further analyzed the primary oxidation products and oxidation mechanism of UDMH in the gas–liquid phase by gas chromatography–mass spectrometry. The results showed as many as 19 oxidation products of UDMH, among which nitroso dimethylamine (NDMA), meta-hydrazone, dimethylamine, water, N, and N-dimethylformamide were the main products. The oxidation of oxygen with gas-phase UDMH significantly increased the production of the potent carcinogen NDMA, in which 30% of the degraded UDMH was converted to NDMA. The mass fraction of NDMA in the gas phase was as high as 1.3%.

In comparison, the production rate of NDMA was about 5% when UDMH interacted with air. Therefore, the failure of UDMH could be avoided by reducing the oxygen content. Bellerby et al. [92] proposed the mechanism of preliminary reaction to form peroxide in low-temperature autooxidation research, which, in turn, led to a chain reaction. However, the effect of these impurities on the combustion performance and the detailed combustion reaction mechanism of the gas phase is unclear.

Fu et al. [93] used DFT to investigate the chemical kinetics of UDMH degradation in wastewater by OH radicals, proposing potential by-products and generation pathways. The study aimed to provide a theoretical foundation for the plasma degradation of UDMH wastewater. It explored the potential of plasma as an advanced oxidation process. The study highlights the importance of considering solvent effects. It identified the rate constants and potential reaction products of UDMH degradation using the M06-2X/6-31G* method in solute electron density (SMD). The significance of OH in decontaminating organic pollutants by plasma was discussed, and the potential applications of plasma in treating UDMH-containing wastewater were highlighted. Further research is needed to fully understand the chemical kinetics of UDMH decomposition by plasma and its potential applications.

Bakaikina et al. [94] described methods for detecting and quantifying toxic chemicals like UDMH. The authors highlight the importance of developing sensitive human health and safety methods. They recommend using solid-phase microextraction and gas chromatography–mass spectrometry with internal standards and standard addition methods to quantify UDMH transformation products accurately and precisely in soil on rocket launch sites. Overall, the studies provide valuable information for environmental monitoring and risk assessment related to rocket launches.

Bukenov et al. [95] studied the use of solid-phase microextraction (SPME) and gas chromatography–mass spectrometry (GC-MS) to detect and quantify transformation products of rocket fuel unsymmetrical dimethylhydrazine (UDMH) in air samples. The study identified several essential transformation products of UDMH in air, including 1,1-dimethylhydrazine, formaldehyde, and acetaldehyde. The authors suggested that this method can help assess the environmental impact of rocket fuels and develop strategies to reduce their impact. However, they noted the need for further research to validate their method and understand the environmental fate and toxicity of UDMH transformation products. The study recommends several future research directions to improve our understanding of UDMH and its impact on human health and ecosystems.

Huang et al. [96] explored the analysis of both intermediate and final products of UDMH (Unsymmetrical dimethylhydrazine) to comprehend the formation of harmful by-products and degradation mechanisms. The investigation involved exposing UDMH solutions to O_3 and examining the resulting degradation samples using SPME-GC/MS. The authors established that the 65 mm PDMS/DVB SPME fiber coating is the most effective at detecting oxidative products of UDMH under certain conditions, at pH 7, a sampling time of 10 min, and a desorption time of 1 min. The study succeeded in identifying the intermediate and final products of UDMH following treatment with O_3 .

Ruomeng et al. [97] studied removing gas-phase unsymmetrical dimethylhydrazine using TiO_2 -reduced graphene oxide aerogel. The study found that moist conditions were conducive to removing gas-phase UDMH, and absorption on TiO_2 -rGA was exothermic. The TiO_2 -rGA showed higher UDMH conversion under UV and VUV light, and the high conversion in a continuous fixed bed reactor indicates the usefulness of this photocatalyst system in removing gas-phase UDMH in practice. The study also noted that chemical interactions and Schottky junction formed in TiO_2 -rGA account for the high charge separation and transmission efficiencies, which help improve catalytic performance. Furthermore, the study confirmed earlier findings regarding the reduction in GO and the slight increase in UDMH conversion to other organics with increased humidity. The article concludes that TiO_2 -rGA is a promising photocatalyst for removing UDMH.

Yi et al. [98] proposed using supercritical water gasification (SCWG) technology to process Unsymmetrical dimethylhydrazine (UDMH), a hazardous waste commonly used as a propellant for military and space programs. They conducted experiments to study the reaction pathways and kinetics of UDMH in supercritical water. They developed a kinetic model for forming gaseous products and ammonia-nitrogen. The study found that SCWG is a practical, resourceful, and harmless utilization technology for UDMH processing. The proposed reaction pathway and kinetic model suggest that UDMH is relatively easy to gasify under supercritical water conditions and can be fully degraded at 400 °C within 3 min without producing nitrate or nitrite.

McNary et al. [99] examined the gas-phase structures of protonated unsymmetrical 1,1-dimethylhydrazine and proton-bound dimers of UDMH and Hydrazine using infrared multiple photon dissociation action spectroscopy. Results show that the proton binds to the methylated nitrogen atom in UDMH, which has two low-lying conformers that are probably populated. The study suggests that the vibrational spectra of such complexes could be helpful in remotely monitoring rocket launches. The authors compared the measured IRMPD spectra to spectra calculated at the B3LYP-GD3BJ/6-311+G(d,p) level of theory to identify the structures present in the experimental studies. The study also explored the thermochemistry and structures of protonated Hydrazine and UDMH and their clusters, utilizing different theoretical methods and basis sets to formulate complete basis set limits.

Xie et al. [100] explored two techniques for detecting leaks of unsymmetrical dimethylhydrazine (UDMH). The first technique involves a newly developed fluorescent, colorimetric sensor with high sensitivity and selectivity but has practical limitations. The second technique uses detection tubes which are cost-effective, easy to use, and provide direct-reading results. However, the detection tube method has a limited detection range. The authors recommend future research to concentrate on miniaturizing and integrating equip-

ment, enhancing detection sensitivity, and creating rapid visual positioning detection methods using new detection materials and portable detectors.

The factors affecting ignition are the vapor pressure, viscosity, surface tension, and density of fluids, along with reaction rates. Blending two fuels can alter their physical properties to achieve desired ignition delays and lower toxicity than hypergolic fuels. Swami et al. [101] stated that bipropellant performance parameters are measured using high-speed cameras and optoelectronic diagnostics. Specific impulse and density-specific impulse were calculated using NASA chemical equilibrium with applications utility. The study found that 2-hydroxyethyl-hydrazine (HEHN) was not hypergolic under normal conditions with oxidizers like dinitrogen tetroxide, WFNA, and RFNA. The ignition delays of hypergolic fuels with WFNA and RFNA were measured, and miscibility with HEHN was estimated. The global ignition delay for UH20 to UH50 blends with RFNA was shown using an optoelectronic circuit. The chemical ignition delays were similar for all blends of UDMH and HEHN and were governed by UDMH. In contrast, physical ignition delays formed a significant component of global delays.

Due to launches, rocket fuel spills are unavoidable, making organizing special impact zones to separate rocket stages containing unconsumed fuel residues necessary. Rodin et al. [102] proposed a method for analyzing unsymmetrical dimethylhydrazine and its transformation products in soil samples using liquid chromatography–mass spectrometry, which involves separating and detecting positive ions. They validated the method using model soils and emphasized the importance of analyzing and detecting UDMH in soil samples to monitor and manage soil contamination. The authors highlighted the need for strict sanitary and hygiene standards to manage soil contamination with unsymmetrical dimethylhydrazine, which is highly hazardous and restricted to a safe impact level of 0.1 mg/kg in soils.

Hu et al. [103] discussed recent advances in pretreatment, analysis, and removal techniques for hazardous pollutants such as unsymmetrical dimethylhydrazine (UDMH) and related compounds. They reviewed various removal techniques and emphasized the need for further research to optimize these techniques for specific applications. The authors reviewed the recent advances in adsorption, catalytic wet peroxide oxidation (CWPO), photocatalytic degradation, biodegradation, and advanced oxidation processes (AOPs) for removing UDMH and related compounds from water or air. The authors recommend carefully optimizing these techniques for specific applications and developing new methods to remove UDMH and related compounds from the environment efficiently.

Smirnov et al. [104] conducted experiments to investigate the catalytic oxidation of unsymmetrical dimethylhydrazine on Pt/SiO₂, identifying intermediate and final reaction products and determining temperature dependencies. They found that platinum has a multifunctional role in the oxidation process. They suggested a new method for detecting unsymmetrical dimethylhydrazine in the air. The study's significance lies in its contribution to understanding the complex catalytic oxidation process on Pt/SiO₂. The findings have implications for detecting and removing unsymmetrical dimethylhydrazine from various environments and emphasize further research.

Yi et al. [105] used molecular dynamics simulations to investigate the gasification mechanism of unsymmetrical dimethylhydrazine (UDMH) in supercritical water. They found that high temperatures favor the free radical degradation reaction pathway. They proposed a mechanism for forming various products due to the oxidation of UDMH. The study confirms previous research on hydrogen production dominating at high temperatures. It identifies the transformation of the element nitrogen in UDMH to nitrogen and ammonia. The study provides valuable insights into resource utilization, highlights the potential harm of improper treatment, and proposes an alternative technology.

Liu et al. [106] conducted an experimental investigation on the combustion and microexplosion of gelled unsymmetrical dimethylhydrazine (UDMH) fuel droplets. It identified three distinct phases and four main phenomena in the combustion process. It includes distinctive combustion stages for freely falling droplets and droplets on a hot plate. The

effects of ambient pressure and oxygen fraction on the burning rate and microexplosions were explored, and theoretical and experimental results were compared and analyzed. Understanding the combustion of single-gelled fuel droplets is crucial in predicting the spray combustion characteristics of high-energy density fuels. The study provides insights into the combustion characteristics of UDMH fuel droplets, aiding in designing high-energy density fuels for optimal performance. However, the study has limitations, such as not fully representing the behavior of larger-scale systems and the need to explore the effects of different gelling agents on combustion characteristics.

Feng et al. [107] discussed research on the burning behavior of gelled UDMH droplets and the effects of oxidizer stream velocity and temperature on flame structure, droplet shape and size, and the burning lifetime of gelled droplets. The study found an increased burning rate constant with pressure and that an open oxidant convective environment significantly affects the gel droplet's burning process. The burning and flame structures were sensitive to the initial velocity of the oxidizer stream. The burning process of the gel droplet was divided into four stages: heating and swelling; bubble nucleation; volume expansion; and microexplosions.

Keshavarz et al. [108] discussed the occupational health risks associated with UDMH, a hydrazine derivative commonly used as a hypergolic propellant. Due to its high vapor pressure, inhalation is the most likely exposure route. Binary mixtures of UDMH and 2-hydroxyethyl hydrazine (HEH) were studied, and it was found that intermolecular attractions between the two compounds contribute to their physical properties. Using binary mixtures of UDMH/HEH offers an improved combination of favorable attributes such as reduced vapor pressure and increased boiling points. Adding HEH, which has a lower vapor pressure and higher boiling point, to UDMH can significantly reduce its hazardous properties.

Sholokhova et al. [109] discussed the limitations of using low-resolution mass spectra for identifying UDMH transformation products. It presented a study that employed machine learning-based prediction of mass spectra and retention indices, in combination with GC-MS and HRMS methods, to improve identification confidence. The study proposed the most confident structures for 24 compounds, including 11 compounds in the NIST database and 13 new compounds. Six new compounds were not previously described as UDMH transformation products. Machine learning methods were used to select the most confident structures based on RI and mass spectra prediction.

Critical Assessment of UMDH Literature

This section presents a comprehensive overview of the research status on UDMH fuel, encompassing oxidation mechanisms, degradation products, detection methods, and potential applications. However, more in-depth analyses of the experimental evidence supporting each theory would significantly enhance our understanding of UDMH oxidation. It is imperative to critically evaluate and compare the different theories, carefully considering the strengths and weaknesses of each, to identify the most plausible mechanisms. To provide a comprehensive understanding, it is essential to conduct a comparative analysis of the sensitivity, selectivity, and applicability of different detection techniques. By critically analyzing the environmental risks and discussing potential mitigation strategies, including their effectiveness and feasibility, we can ensure the safe and responsible application of UDMH fuel.

3. Discussion

The updated mechanism by Konnov et al. [36] shows the importance of efficient thermochemistry prediction, and this can be achieved through high-level quantum calculation and other advanced computational methods. The formation of Ammonia (NH_3) from N_2H_4 and NH_2 , as shown in Figure 3, shows a similar trend from lower temperatures rising steadily to higher temperatures. However, the rate constants, as estimated by the two compared studies, show a difference of various orders of magnitude. The H-atom

abstraction reactions of N_2H_4 with H and NH_2 , as shown in Figures 3 and 4, show a steady rise in the rate constant as temperature increases. However, two different rate constants estimation show quite a difference with an order of magnitude difference. This confirms the need for more theoretical and experimental studies to develop a validated mechanism that can accurately predict the behavior of hydrazine-based fuels under different temperature and pressure conditions.

Regarding oxidation mechanisms, the literature presents different theories regarding converting UDMH to nitroso dimethylamine (NDMA). Evaluating and comparing these theories is crucial to determine the most plausible oxidation mechanism for UDMH. Further research is needed to investigate multiple reaction pathways under the simultaneous action of various oxidants to accurately determine the main pathways for NDMA formation from UDMH in the atmosphere.

Second, regarding detecting UDMH and its transformation products, a range of techniques has been employed. However, there is a need for critical evaluation and comparison of these methods. By thoroughly assessing each detection technique's sensitivity, selectivity, and applicability, researchers and practitioners can choose the most suitable method for their specific requirements. This would significantly enhance the accuracy and reliability of UDMH detection and contribute to effective monitoring and management of soil and air contamination. Future studies should focus on conducting comparative analyses to determine the strengths and limitations of different detection methods, enabling the selection of the most appropriate approach.

Furthermore, the environmental risks associated with UDMH necessitate careful evaluation and the development of effective mitigation strategies. The literature highlights the importance of conducting risk assessments and implementing measures to minimize the impact of UDMH on human health and ecosystems. However, there is a lack of critical analysis and discussion in this area. To address this gap, it is essential to thoroughly examine the environmental risks and evaluate the effectiveness of current mitigation measures. By doing so, researchers and policymakers can make informed decisions to ensure the safe and responsible application of UDMH fuel. Additionally, future research should focus on identifying novel mitigation strategies and exploring their feasibility and effectiveness.

4. Conclusions

This review summarized recent advances in the kinetics and reaction mechanisms of the thermal decomposition reactions of three hydrazine-based self-ignition propellants. Key experimental data for hydrazine/NTO are missing due to the self-ignition characteristics. Some of the available chemical reaction kinetic mechanisms of hydrazine propellants in the literature ($\text{N}_2\text{H}_4/\text{NTO}$, MMH/O_2 , and MMH/NTO) have missing reaction paths and thermodynamic parameters to varying degrees. Some reaction rate constants are only obtained by estimation. The mechanisms are narrowly applicable and can hardly meet the current needs. The following key points could be highlighted:

(1) The highly reactive reaction of N_2H_4 and NO_2 is caused by the continuous H-atoms abstraction from N_2H_4 by NO_2 , $\text{N}_2\text{H}_4 \Rightarrow \text{N}_2\text{H}_3 \Rightarrow \text{N}_2\text{H}_2 \Rightarrow \text{NNH} \Rightarrow \text{N}_2$, in which a large amount of heat is released during this process, especially by the reaction that produces N_2 , and the temperature increase accelerates the reaction $\text{N}_2\text{H}_4 \Rightarrow \text{N}_2\text{H}_3$ with a small activation potential;

(2) The overall decomposition rate of MMH is consistent with first-order kinetics. N-N bond splitting is the most sensitive reaction pathway to simulate the homogeneous decomposition of MMH at high pressure, with pressure dependence at 0.3 to 5 atm. The measured reaction rate constants follow a pressure-dependent trend. In addition, simple C-N bond fission to generate radicals $\text{CH}_3 + \text{NHNH}_2$ is also expected to dominate the decomposition kinetics. NO_2 continues to abstract H atoms on the intermediate N of MMH at low temperatures to generate products (CH_3NNH_2 and HONO), followed by exothermic

HONO cleavage to generate $\dot{\text{O}}\text{H}$ radicals, which is the main reaction that induces ignition. H-atom abstraction by $\dot{\text{O}}\text{H}$ radicals and $\dot{\text{H}}$ are also essential to the MMH reaction kinetics;

(3) UDMH will slowly oxidize or decompose to produce up to 19 trace oxidation products during long-term storage, of which nitroso dimethylamine (NDMA), unsymhydrazine, dimethylamine (FDMH), water, and *N, N*-dimethylformamide (DMF) are the main products. However, the mechanism and pathway of converting UDMH to NDMA are not precise. The dominance of the oxygen addition reaction or the hydrogen capture reaction in the oxidation of UDMH to NDMA is also further discussed.

A detailed kinetic study of the reaction mechanism of UDMH has not been seen in the available studies. In as much as there is a need for a detailed kinetic study of these fuels, there is also a need to develop more safe and sustainable alternatives for propellant and fuel applications.

Author Contributions: J.W. and Y.L. supervised the project and the provision of financial resources. F.N.O.B. was responsible for the overall conceptualization of the study, the graphical and tabular representations, and the writing and editing of the final draft. X.B. and X.R. contributed equally to this work by developing the initial development of manuscript and literature sources for hydrazine fuels. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge the funding support from the: Startup Funds of Aoxiang Overseas Scholar from Northwestern Polytechnical University (0602022GH02002135).

Data Availability Statement: Not applicable.

Acknowledgments: The authors thank Esther Chota (Chang'an University) and Sandra Asante (Xi'an Jiaotong University) for their insightful discussions on environmental sustainability.

Conflicts of Interest: The authors declare no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

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