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Study on the Ignition Delay Time of n-Heptane Fuels

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Abstract. As a basic standard for gasoline anti-knock performance, the ignition delay time (IDT) of n-hexane is essential for optimizing internal combustion engine efficiency and lowering pollutants. IDT is an essential metric in combustion research because it represents the reactivity of fuels under different thermodynamic circumstances and offers critical benchmarks for confirming chemical kinetic models. This study investigated n-heptane IDT using experimental approaches (shock tube, rapid compression machine (RCM), spherical bomb) and kinetic modeling (Curran's detailed mechanism, Peters' skeletal models). By combining laboratory-scale measurements with numerical simulations, the study establishes a more comprehensive picture of ignition behavior. Effects of fuel blending (H_2, n-butanol), EGR dilution, and surrogate fuels are examined. Key findings include: H_2 prolongs IDT by ~27% in the NTC region; n-butanol affects IDT through OH radical competition; a ternary surrogate (63% iso-octane/20% toluene/17% n-heptane) replicates gasoline IDT within 10%. Data for < 600 K or > 30% EGR are limited, cross-reactions are frequently disregarded, and simplified processes differ in NTC-region predictions. All things considered, this work supported international initiatives to lower emissions associated with combustion and enhance engine design techniques by strengthening the connection between experimental combustion research and kinetic modeling and offering insights for the production of cleaner fuels.

Keywords: New energy, n-heptane, Ignition Delay Time

1. Introduction

As the zero-point standard on the octane rating scale is n-hexane (C_7H_{16}) and iso-octane is 100, it is an essential reference fuel that is commonly used to evaluate the anti-knock performance of gasoline. For diesel, automotive, and aviation applications, its combustion properties are crucial because they enhance environmental performance by generating comparatively lower CO_2 emissions. A high-temperature ignition delay time (IDT), or the time between fuel injection and spontaneous ignition, is essential for optimizing combustion efficiency and minimizing pollution production. Engineers can improve engine thermal efficiency, decrease emissions of unburned hydrocarbons, and modify ignition time by having a solid understanding of n-heptane's IDT. The significance of comprehending n-heptane behavior at different temperatures and pressures is further shown by molecular dynamics simulations. N-heptane IDT research contributes to the creation of

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cleaner, more efficient fuels and is in line with international initiatives to reduce the negative effects of combustion on the environment.

With an emphasis on the NTC region, which is crucial for diesel engines, Comandini et al. [1] used a reflected shock tube to measure the ignition delay times of n-heptane/hydrogen/air mixtures at 20 bar and 730–1200 K. They verified their findings using the Cai and Pitsch kinetic model. By creating synthetic EGR ($O_2/N_2/CO_2/H_2O/Ar$) and simplifying formulations, Desantes et al. [2] laid the foundation for studies pertaining to buffer gases by simulating how EGR components impact n-heptane ignition delay, differentiating between thermal (heat capacity) and chemical effects using CHEMKIN. In addition to Desantes' EGR component analysis, Di et al. [3] isolated thermal and chemical (third-body collision efficiency) effects on n-heptane ignition using a rapid compression machine (RCM) at 600–850 K with N_2/Ar/Ar-CO_2 buffer gases. Lean n-heptane/air mixtures (720–1100 K, 50 bar) were tested by Herzler et al. [4] using a shock tube. They observed NTC behavior and two-stage ignition, verifying results with Curran's mechanism and providing a foundation for high-pressure lean mixture ignition studies.

To extend Herzler's single-fuel shock tube work to blends, Gauthier et al. [5] performed shock tube experiments on n-heptane/gasoline/surrogate blends (850–1280 K, 15–60 atm). They confirmed that a ternary surrogate (iso-octane/toluene/n-heptane) matches gasoline ignition delay. Zhang et al. [6], in connection with Gauthier's blend research, measured the ignition delay of n-heptane/n-butanol mixtures using a shock tube (1200–1500 K, 2/10 atm) and combined Curran's n-heptane mechanism with n-butanol submodels to investigate OH radical competition between fuels. Curran's intricate n-heptane mechanism was simplified by Peters et al. [7] into 30-step and 4-step skeletal versions. They also identified rate-determining reactions, such as ketohydroperoxide dissociation, and derived analytical solutions for ignition delay across temperature regimes. Comandini, Zhang, and Peters all used the detailed n-heptane mechanism (1034 species, 4238 reactions) developed by H.J. Curran et al., validated via shock tube and RCM data, to simulate ignition and improve their models. This body of work provides a coherent research framework focused on kinetic simulation and experimental measurement while highlighting existing gaps, such as deviations of simplified models in the NTC region, scarcity of low-temperature data (<600 K), limited EGR studies (>30%), and overlooked cross-reactions.

Existing research on n-heptane ignition delay exhibits several limitations. Predictions in the NTC region often deviate from simplified kinetic mechanisms because these models omit small but crucial reactions. Moreover, cross-reactions between n-heptane and substances such as CO_2 or n-butanol are frequently neglected in studies involving EGR or fuel blends. Data remain scarce under extreme conditions, particularly at very low temperatures (<600 K) or with high EGR levels (>30%) in shock tube and RCM experiments. To address these shortcomings, future work should focus on improving kinetic mechanisms by incorporating relevant cross-reactions into Curran’s model, closing data gaps for harsh conditions through targeted RCM and shock tube studies, and validating results across different experimental facilities. Such efforts will enhance the reliability of models, particularly for dual-fuel and high-EGR engine applications.

2. Advances in n-heptane ignition delay time studies

Through a combination of chemical kinetic modeling and experimental studies, the ignition delay time (IDT) of n-heptane has been thoroughly investigated, leading to a systematic framework that covers a variety of combustion circumstances, fuel blends, and diluent effects. High-temperature and high-pressure IDT measurements are mainly performed using shock tubes. Comandini et al. [1] examined n-heptane/H_2/air mixtures in both a spherical bomb for laminar flame speed (LFS)

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measurements at 294 K and 1 bar, and a reflected shock tube for IDTs at 20 bar and 730–1200 K. Their experiments demonstrated that hydrogen has little effect on high-temperature IDTs but significantly prolongs IDTs in the negative temperature coefficient (NTC) region by up to 27% at 75% H_2. This effect is attributed to the reduced n-heptane concentration suppressing low-temperature chain branching, such as ketohydroperoxide formation. The Cai-Pitsch kinetic model (236 species) was able to reproduce experimental results with less than 5% error, indicating that hydrogen enhances radical formation without altering the primary n-heptane oxidation pathways. Similarly, Herzler et al. [4] studied lean n-heptane/air mixtures (Φ=0.1–0.4, 720–1100 K, 50 bar) and observed two-stage ignition below 900 K, with pre-ignition behavior largely independent of equivalence ratio, while main ignition delays increased as the mixture became leaner. Their results were consistent with Curran's detailed mechanism (1034 species), although minor adjustments in rate constants were needed at higher temperatures.

Rapid compression machines (RCMs) complement shock tube studies by providing high-resolution data in low-temperature regions and capturing the complex NTC behavior. Di et al. [3] employed a creviced-piston RCM to study the thermal and chemical effects of buffer gases (N_2, Ar, and Ar–CO_2 mixtures) on n-heptane IDTs between 600 and 850 K. They found that thermal effects dominated IDT variations in the NTC region, accounting for approximately 80% of the differences between Ar and N_2, while CO_2's chemical effect, such as enhanced third-body efficiency in H_2O_2 decomposition, became significant above 850 K, reducing IDTs by roughly 15%. Additional studies on diluents and EGR, such as those by Desantes et al. [2], highlighted the significant roles of CO_2 and H_2O in determining IDTs, while Ar could be neglected for low O_2 fractions.

Using shock tube-based IDT research, Gauthier et al. [5] examined n-heptane, RD387 gasoline, and a ternary surrogate (63% iso-octane/20% toluene/17% n-heptane by volume) at HCCI-relevant settings (850–1280 K, 15–60 atm, 0–30% EGR). Their findings supported the strong NTC behavior of n-heptane, which is in line with Herzler et al. [4]. Crucially, the ternary surrogate faithfully reproduced gasoline IDTs at all equivalence ratios (Φ=0.5, 1.0, 2.0): rich mixtures (Φ=2.0) displayed indistinguishable IDTs at low pressures but shorter ones at high pressures, while lean mixtures (Φ=0.5) had longer IDTs than stoichiometric ones at both low (15–25 atm) and high (45–60 atm) pressures. With a greater impact at lower temperatures, ascribed to O_2 dilution and inhibited radical formation, EGR addition extended IDTs for both gasoline and the surrogate, confirming the surrogate's usefulness for engine-relevant simulations.

Zhang et al. [6] employed a shock tube (1200–1500 K, 2/10 atm, Φ=0.5/1.0) and an RCM (700–907 K, 20 atm) to study n-heptane/n-butanol mixes (neat n-heptane, 80/20, 50/50, 20/80, neat n-butanol). Because of increased β-scission-driven radical generation, IDTs rose linearly with n-butanol content at high temperatures (neat n-butanol had the shortest IDTs). IDTs increased nonlinearly at low temperatures: pure n-butanol showed longer IDTs and no NTC trend because its OH group promoted the generation of α-hydroxybutyl radicals (via reaction R2915: $C_4H_8OH\text{-}1 + O_2 \rightarrow NC_3H_7CHO + HO_2$) over low-temperature chain branching (QOOH creation).The struggle between n-heptane and n-butanol for OH radicals, which prevented n-heptane consumption while encouraging n-butanol's oxidation, was captured by a combined kinetic model (Curran's n-heptane mechanism + Sarathy's n-butanol model), which recreated IDTs with a <10% inaccuracy.

To improve kinetic modeling, Peters et al. [7] reduced a 56-step skeletal mechanism to a 30-step short mechanism that included two n-heptyl radical isomers. They then went on to create 4-step global mechanisms that were suited to low, moderate, and high temperature regimes. The 30-step system accurately reproduced IDTs at temperatures and pressures ranging from 1 to 100 bar. Drivers peculiar to a regime were identified by analytical solutions: Reactions 11/15 at low temperatures

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(<800 K) depended on the breakdown of ketohydroperoxide (KET), which had an overall activation energy of 125.6 kJ/mol (average of E_{11} and E_{15}); High temperatures (>1000 K) relied on H_2O_2 decomposition (reaction 30), with activation energy associated with three key reactions; intermediate temperatures (800–1000 K) featured a temperature cross-over (T*) where α (fraction of heptyl radicals in low-temperature chains) dropped below 0.5, shifting from chain branching to breaking, with IDTs governed by H_2O_2 dissociation. This simplification supported engineering-scale simulations by striking a compromise between computational efficiency and kinetic accuracy.

With Curran's mechanism serving as a unifying framework, current studies, which span 600–1500 K and 2–60 bar, clarify that n-heptane IDT is controlled by the thermal (heat capacity) and chemical (radical generation) effects of diluents/blends. Although cross-reactions between n-heptane and oxygenates and ultra-low T (<600 K) data still have gaps, the work that has already been done offers reliable data for high-EGR and dual-fuel engine combustion optimization.

3. Critical evaluation of experimental and modeling approaches

Current n-heptane research demonstrates notable strengths in both experimental design and modeling reliability. Spherical bomb experiments enable precise laminar flame speed measurements, capturing flame propagation in dual-fuel mixtures with high-speed Schlieren imaging, which allows accurate calculation of Markstein lengths. Shock tubes are capable of replicating high-pressure and lean combustion conditions relevant to diesel and dual-fuel engines, while RCMs allow detailed observation of low-temperature NTC behavior, which is critical for HCCI combustion studies. Synthetic EGR setups provide realistic simulation of engine exhaust compositions, allowing systematic investigation of EGR and diluent effects on IDTs. Furthermore, detailed chemical kinetic models, including those by Curran et al. [4,6] and Cai and Pitsch [1], can predict experimental results within 5% error, and skeletal mechanism reductions by Peters et al. maintain key reaction pathways for engine-relevant simulations. By ensuring that gasoline surrogates closely resemble real fuel IDTs across pressures, temperatures, and EGR levels, surrogate fuel validation—as carried out by Gauthier et al. [5]—provides a useful benchmark for engine optimization.

Despite these advantages, there are still a few drawbacks. Long ignition delays and ultra-lean mixes (Φ<0.1) are difficult to evaluate using shock tube tests due to their short test durations (e.g., <15 ms). RCM heat losses, even when minimized with creviced pistons, can reduce post-compression temperatures by several Kelvin, affecting low-temperature IDTs, particularly in the NTC region. Narrow parameter ranges, such as Φ=1 or T<1500 K, limit the generalizability of current findings to high-load engines or extreme stoichiometries. Simplifications in kinetic mechanisms, such as the omission of cross-reactions and trace species, lead to overprediction or underprediction of IDTs in blended fuels or EGR applications. For example, ignoring n-heptyl-butanol radicals or NO/CO interactions in EGR models can result in errors exceeding 5–10%, highlighting the need for comprehensive data coverage and more complete modeling frameworks. All of these flaws point to the need for more improvements in order to achieve forecast accuracy in complicated engine circumstances, even if the current body of research offers a strong basis.

4. Strategies for enhancing experimental precision and model reliability

Several tactics can be used to improve kinetic model completeness, increase experimental precision, and broaden data coverage in order to overcome the shortcomings in the existing n-heptane study.

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4.1. Experimental apparatus: enhancing precision and extending capabilities

4.1.1. Shock tube test time and ignition localization optimization

Herzler et al. [4] noted that standard shock tubes, with test durations below 15 ms, limit the measurement of long ignition delay times (IDTs) for ultra-lean n-heptane mixtures. Hartmann et al. [8] addressed this by employing a customized Ar/He driver gas (6.2–12.5% Ar in He) to match acoustic impedance, thereby extending the effective test time to 15 ms. Further refinement is possible by increasing the test duration to 20 ms and adjusting the Ar/He ratio to 8–15%, enabling accurate IDT measurements for ultra-lean mixtures ($\Phi < 0.1$), a regime not explored by Herzler et al. In addition, Hartmann et al. utilized ICCD imaging to confirm ignition localization at the shock tube center. By combining this with fiber-optic pressure sensors with 1 mm spatial resolution, the accuracy of IDTs for two-stage ignition in the NTC region can be significantly improved, mitigating sidewall diagnostic errors previously observed by Di et al. [3].

4.1.2. RCM heat loss reduction and low-temperature sensing

Although the crevice-piston design in Di et al.'s RCM [3] reduces heat loss, slight post-compression temperature drops (<5 K) still occur. To further minimize heat loss to under 2 K, a heated reaction chamber maintained at 323 K combined with a double-layer insulated piston (aluminum core with ceramic covering) is recommended. Incorporating laser-induced fluorescence (LIF) for OH radical detection with the Ar/CO_2 buffer gas technique enhances low-temperature ignition measurements (<600 K). This approach addresses the limitations in Zhang et al.'s n-heptane/n-butanol study [6], where weak NTC behavior could not be fully resolved using conventional pressure transducers, thereby enabling more precise low-temperature IDT determination.

4.1.3. MBMS sampling range expansion

Hartmann et al.'s [8] molecular-beam mass spectrometer (MBMS) could not probe regions below 0.5 mm above the burner, missing critical near-burner radical profiles. By reducing the quartz sampling nozzle aperture from 0.1 mm to 0.05 mm and integrating Raman spectroscopy, it becomes feasible to measure species such as H_2O and CO_2 in situ within this near-burner region. This modification allows for complete flame structure characterization from burner surface to exhaust, complementing Hartmann et al.'s data on EHN-doped n-heptane flames and providing a more comprehensive understanding of combustion dynamics.

4.2. Chemical kinetic model: refining completeness and applicability

Peters et al.'s 30-step skeletal mechanism [7] overpredicted IDTs by approximately 10% due to omission of minor but significant cross-reactions, such as interactions between n-heptyl and butanol radicals. In studies of PRF blends (n-heptane/iso-octane), AlAbbad et al. [9] found that current models often fail to capture the coupled temperature-pressure dependence of IDTs in the NTC region. This limitation can be addressed by incorporating cross-reactions between n-heptane and iso-octane radicals (e.g., $C_7H_{15} + C_8H_{17} \rightarrow C_7H_{16} + C_8H_{16}$), with rate constants calibrated against PRF 70–95 IDT data [10]. Additionally, rate constants from Comandini et al.'s Cai and Pitsch model [1], which accurately predicted laminar flame speeds of n-heptane/hydrogen mixtures, can be employed to account for H-abstraction reactions between n-heptane and hydrogen radicals.

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Maroteaux et al. [11] proposed a 7-step n-heptane mechanism coupled with a temperature criterion (T_fr = 292 + 9ε - 40p_inlet + …) to predict ignition timing in HCCI combustion, highlighting the importance of integrating chemical kinetics with engine operating parameters. Applying this criterion to EGR modeling addresses the underprediction of IDT reductions at >30% EGR in Desantes et al.'s work [2], where NO/CO reactions were neglected. Incorporating NO_x-hydrocarbon reactions (e.g., NO + QOOH → NO_2 + alkene) from Hartmann et al. [8] and CO oxidation pathways (CO + OH → CO_2 + H) ensures that synthetic EGR ($O_2/N_2/CO_2/H_2O$/NO) can reproduce real-engine IDTs with errors below 1%. For high-pressure scenarios (>40 atm), optimization of pressure-dependent reactions, such as H_2O_2(+M) → 2OH (+M) [10], further enhances model accuracy for heavy-duty engine conditions.

4.3. Parameter range: expanding engine relevance and data coverage

4.3.1. Broadening equivalence ratio and additive concentration

Herzler et al. [4] investigated only Φ = 0.1–0.4, omitting ultra-lean (Φ < 0.1) and rich (Φ > 2.0) regimes. AlAbbad et al. [9] demonstrated that rich mixtures exhibit distinct NTC behavior relevant to direct-injection diesel engines. To comprehensively map reactivity, n-heptane tests should be extended to Φ = 0.05–3.0, similar to Hartmann et al.'s approach for EHN concentrations (0.01–1%) [8]. Zhang et al.'s n-butanol studies [6,11] lacked additive concentration-gradient data; this can be addressed by testing concentrations from 0.001–5% and applying Maroteaux et al.'s temperature criterion to quantify the effect of EHN dosage on ignition timing under HCCI conditions (e.g., 750 K, 20 atm).

4.3.2. Supplementing high-temperature/pressure data and HCCI-specific conditions

Zhang et al. [6] lacked IDT measurements above 1500 K, critical for high-load engines. Utilizing a heated shock tube capable of 1800 K, combined with Hartmann et al.'s driver gas adjustments [8], allows measurements at 1500–2000 K and 60–100 atm. For HCCI-relevant low temperatures (600–800 K), integrating Di et al.'s RCM data [3] with Maroteaux et al.'s 7-step mechanism [11] generates IDT data for ultra-lean mixtures (Φ = 0.2–0.4) with 0–60% EGR, addressing gaps in ultra-lean regimes and supporting the design of HCCI engine control strategies [4].

5. Conclusion

This study systematically investigated n-heptane (C_7H_{16}) ignition delay time (IDT)—a critical parameter for internal combustion engine optimization—through both experimental and modeling approaches. Experiments using shock tubes, rapid compression machines (RCMs), and spherical bombs spanned 600–1500 K and 2–60 bar, examining the effects of fuel blending, EGR dilution, and buffer gases. Key findings include: hydrogen prolongs NTC-region IDTs by ~27% at 75% H_2 by suppressing low-temperature chain branching; n-butanol extends high-temperature IDTs linearly (e.g., 80% n-butanol causes 40% prolongation at 1200 K, 10 bar) and affects low-temperature IDTs nonlinearly via OH radical competition; a ternary surrogate fuel (63% iso-octane / 20% toluene / 17% n-heptane) reproduces gasoline IDTs within 10% accuracy. Modeling efforts validated Curran's detailed mechanism (1034 species) and Peters' simplified 4-step model, which identifies rate-determining reactions such as ketohydroperoxide decomposition in low-temperature regions. Additionally, buffer gas studies revealed that thermal effects dominate NTC-region IDT variations (~80% for Ar vs N_2), while CO_2 introduces a ~15% chemical reduction in IDTs above 850 K.

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The study also identified several limitations: shock tubes with maximum 15 ms test times cannot capture ultra-lean (<Φ 0.1) or ultra-low-temperature (<600 K) IDTs; RCM heat losses introduce errors in low-temperature measurements; kinetic models omit important cross-reactions (e.g., n-heptyl–butanol radical interactions) and trace species (NO_x), causing predictive biases. Future work should extend shock tube test times to 20 ms, incorporate cross-reactions into kinetic models, and expand measurements to high-EGR (>30%) and high-temperature (>1500 K) regimes to improve engine-relevant predictions.

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