Autoignition study of tetralin in a rapid compression machine at elevated pressures and low-to-intermediate temperatures

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HIGHLIGHTS

- Ignition delays of tetralin/O_2/N_2 mixtures at high pressures were measured.
- Pre-ignition heat release was observed at low temperatures.
- No evidence of negative temperature coefficient behavior was observed.
- Improvements to model suggested based on experiments and chemical kinetic analyses.

ARTICLE INFO

ABSTRACT

Tetralin (1,2,3,4-tetrahydronaphthalene) is a naphtheno-aromatic compound found in diesel fuels and a candidate component widely used in diesel surrogates. The fundamental understanding of the autoignition characteristics of tetralin is meager due to the lack of experimental and computational studies in the literature. Considering this, an experimental study using a rapid compression machine (RCM) has been conducted to investigate the ignition characteristics of tetralin at varying pressures from 15 bar to 50 bar, temperatures between 762 K and 950 K, and equivalence ratios of ϕ = 0.5 and 1.0. The effect of dilution on ignition delay times was also studied by varying the initial concentrations of oxygen and tetralin independently. Furthermore, the test conditions investigated in the current study were designed to provide ignition delay measurements complementary to the literature data. A comparison of the ignition delays measured from the current study with those existing in the literature demonstrated consistent trends and good agreement. Examination of the RCM pressure histories showed that while tetralin does not exhibit two-stage ignition behavior, some evidence of pre-ignition heat release was noticed at the low temperature conditions investigated in the study. Further comparison with experimentally measured ignition delays of *n*-butylbenzene was conducted to demonstrate the effect of molecular structure on the autoignition properties. Chemical kinetic simulations carried out to assess the performance of an available kinetic model showed this model to be significantly less reactive than the experiments. Brute force sensitivity analyses and reaction pathway analyses were further conducted at varying pressures, temperatures, and equivalence ratios to identify the controlling chemistry. Possible reasons for the poor performance of this chemical kinetic model in predicting the experimental ignition delays have been discussed based on experimental results and chemical kinetic analyses from the current study.

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1. Introduction

1,2,3,4-Tetrahydronaphthalene, commonly known as tetralin, is a naphtheno-aromatic hydrocarbon found in diesel fuels. As such, tetralin has been proposed as a constituent in simplified fuel blends, known as surrogate fuels [1], designed to emulate the properties of real diesel fuel. Typically, a model describing the chemical kinetics of a real fuel is generated by hierarchically merging the chemical kinetic models of each of the constituents of the surrogate for the target real fuel. Therefore, it is necessary to develop high fidelity chemical kinetic models for each of the surrogate constituents. The chemical kinetic models developed to describe the combustion chemistry of the surrogates need to be validated against fundamental experimental data such as ignition delays from rapid compression machines (RCMs) and shock tubes, species

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measurements from jet stirred reactors (JSRs) and flow reactors, and laminar flame speed measurements. To date, very few studies [2–4] have focused on studying the fundamental combustion characteristics of tetralin. Yang and Boehman [2] studied ignition characteristics of tetralin in a CFR engine and compared the ignition propensity of tetralin with those of methylcyclopentane and decalin. Yang and Boehman [2] also conducted a detailed product analysis to understand the important reaction pathways of tetralin oxidation. From the product analysis, Yang and Boehman [2] concluded that tetralin does not exhibit low temperature chemistry and that the oxidation of tetralin is dominated by dehydrogenation reactions leading to formation of dialin and naphthalene. Wang et al. [3] measured ignition delays of tetralin/air mixtures using a shock tube at equivalence ratios of ϕ = 0.5 and 1, and at pressures of 13 bar and near 38 bar for temperatures between 978 K and 1277 K. Dagaut et al. [4] studied the oxidation characteristics of diluted tetralin/oxidizer mixtures in a JSR, with the initial concentration of tetralin at 1000 ppm, in the temperature range of 800–1400 K, at varying pressures between 1 atm and 10 atm, and over a range of equivalence ratios between 0.5 and 1.5.

In addition to the oxidation studies, the pyrolysis of tetralin has been studied by several researchers [5–9]. Tsang and Cui [5] studied pyrolysis of tetralin in a shock tube in the temperature range of 1000–1400 K by measuring concentrations of products formed due to unimolecular decomposition and hydrogen atom induced decomposition. Using the concentrations of the pyrolysis products, Tsang and Cui [5] determined rate constants of several decomposition reactions and reactions of tetralin with hydrogen radical. Yu and Eser [6] studied the pyrolysis chemistry of tetralin and decalin at near-critical and supercritical conditions. For the conditions investigated in their study, Yu and Eser [6] found 1-methylindan and naphthalene to be the dominant products with the yield of the former being always greater than the latter. Stewart et al. [7] studied supercritical pyrolysis of tetralin in a specially constructed flow reactor at varying pressures between 0.2 MPa and 10 MPa and varying temperatures between 700 K and 810 K. Stewart et al. [7] observed 1-methylindan, naphthalene, and *n*-butylbenzene to be the major products of supercritical pyrolysis of tetralin. Li et al. [8] studied pyrolysis of tetralin using a flow reactor at low pressures of 30 Torr and at varying temperatures from 850 K to 1500 K. Pyrolysis products were identified using synchrotron vacuum ultraviolet photoionization mass spectrometry, and Li et al. [8] concluded that tetralin pyrolysis is dominated by unimolecular decomposition and H-abstraction reactions at low pressures. Li et al. [8] also developed a kinetic model consisting of 149 species and 554 reactions that describes the pyrolysis chemistry of tetralin. Zámostný et al. [9] studied pyrolysis of tetralin along with fifty-five other hydrocarbon molecules at a temperature of 810 °C, pressure of 400 kPa, and residence times of 0.2–0.4 s. Naphthalene was found to be the major product from pyrolysis of tetralin for the conditions investigated by Zámostný et al. [9].

Only one model describing the oxidation kinetics of tetralin has been presented in the literature to our knowledge. In the work of Dagaut et al. [4], their chemical kinetic model was found to predict the ignition delays from the shock tube work of Wang et al. [3], the speciation measurements from the JSR work of Dagaut et al. [4], and the pyrolysis data of Li et al. [8] and Zámostný et al. [9] to a reasonable agreement.

The objective of the current study is to investigate the autoignition characteristics of tetralin at low-to-intermediate temperatures and elevated pressures using an RCM. These engine-relevant conditions have not been extensively studied in the literature. Further, the high quality experimental data from the RCM will be compared with the simulated results using the chemical kinetic model from the work of Dagaut et al. [4]. In addition, several chemical kinetic analyses of the model will be conducted to elucidate the underlying mechanics of the autoignition delay predictions under the conditions of the present experiments. In the following, we will sequentially detail the experimental specification, test conditions, experimental results, model performance assessment, and chemical kinetic analyses and discussion.

2. Experimental facility

2.1. Experimental procedure

The RCM at the University of Connecticut has been described extensively by Das et al. [10]. It employs a creviced piston to compress test mixtures to elevated pressures and temperatures. The creviced piston was specially designed following the work of Mittal and Sung [11] to effectively suppress the effects of roll-up vortex and ensure that an adiabatic core region of gas is maintained throughout the experimental duration. Moreover, Das et al. [12] and Uddi et al. [13] have shown that the temperature distribution of the core region is adequately homogeneous prior to hot ignition. The piston is driven pneumatically and brought to rest by a hydraulic pin-groove mechanism towards the end of the compression stroke. While the typical compression times are around 30–45 ms, the majority (>50%) of pressure/temperature rise occurs in the last 6 ms of compression, as shown in Fig. 1. A trigger from LabVIEW® initiates the compression event and starts data acquisition. Dynamic pressure in the reaction cylinder is measured using a thermal-shock resistant Kistler 6125C transducer in conjunction with a 5010B charge amplifier. A test gas mixture can be compressed to the desired test condition at the end of compression, represented by compressed pressure (P_C) and compressed temperature (T_C), by independently varying the geometric compression ratio, initial pressure (P_0), and initial temperature (T_0). Geometric compression ratios varying between 7 and 17 can be attained by varying the piston stroke length and/or the end of compression (EOC) clearance length. Moreover, the compressed temperature is deduced from the measured pressure trace by applying the adiabatic core hypothesis and the assumption of isentropic compression: $\int_{T_0}^{T_C} \frac{\gamma}{\gamma-1} \frac{dT}{T} = \ln\left(\frac{P_C}{P_0}\right)$, where γ is the specific heat ratio of the test mixture and is a function of temperature.

Prior to the start of an experiment, the reaction chamber is filled to the desired intake pressure with a homogenous fuel/oxidizer mixture prepared in a separate stainless steel mixing chamber. The mixing chamber, the RCM reaction chamber, and all connecting manifolds are equipped with heaters to preheat the mixture uniformly to the desired initial temperature. In the current study, tetralin (99% purity), supplied by Sigma-Aldrich, and ultra-high purity (>99.99%) O_2 and N_2 from Airgas were used to prepare homogenous tetralin/oxidizer mixtures in the mixing chamber. Tetralin was injected into the mixing chamber on a gravimetric basis using a
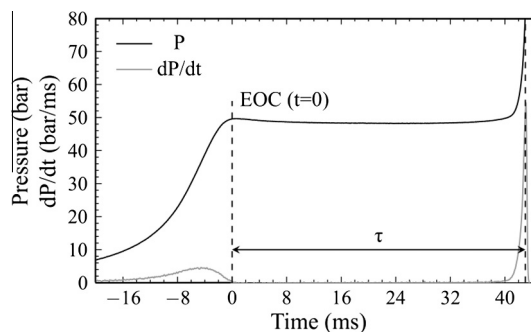

Fig. 1. Definition of ignition delay. Experimental conditions: tetralin/O_2/N_2 = 0.8/20.84/78.36 by mole, P_0 = 2125 Torr, T_0 = 380 K, P_C = 50 bar, T_C = 796 K, and τ = 43 ms.