



An updated experimental and kinetic modeling study of *n*-heptane oxidation



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ABSTRACT

This work presents an updated experimental and kinetic modeling study of *n*-heptane oxidation. In the experiments, ignition delay times of stoichiometric *n*-heptane/air mixtures have been measured in two different high-pressure shock tubes in the temperature range of 726–1412 K and at elevated pressures (15, 20 and 38 bar). Meanwhile, concentration versus time profiles of species have been measured in a jet-stirred reactor at atmospheric pressure, in the temperature range of 500–1100 K at $\phi=0.25, 2.0$ and 4.0. These experimental results are consistent with those from the literature at similar conditions and extend the current data base describing *n*-heptane oxidation.

Based on our experimental observations and previous modeling work, a detailed kinetic model has been developed to describe *n*-heptane oxidation. This kinetic model has adopted reaction rate rules consistent with those recently developed for the pentane isomers and for *n*-hexane. The model has been validated against data sets from both the current work and the literature using ignition delay times, speciation profiles measured in a jet-stirred reactor and laminar flame speeds over a wide range of conditions. Good agreement is observed between the model predictions and the experimental data. The model has also been compared with several recently published kinetic models of *n*-heptane and shows an overall better performance. This model may contribute to the development of kinetic mechanisms of other fuels, as *n*-heptane is a widely used primary reference fuel. Since the sub-mechanisms of *n*-pentane, *n*-hexane and *n*-heptane have adopted consistent reaction rate rules, the model is more likely to accurately simulate the oxidation of mixtures of these fuels. In addition, the successful implementation of these rate rules have indicated the possibility of their application for the development of mechanisms for larger hydrocarbon fuels, which are of great significance for practical combustion devices.

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1. Introduction

The oxidation of *n*-heptane has been widely studied as it is a primary reference fuel (PRF) and is a representative normal alkane. It is also an important component of toluene reference fuel (TRF) and ethanol toluene reference fuel (ERF) [1], which has been used as a surrogate gasoline fuel for research of combustion processes in internal combustion engines [2]. Experiments have been performed which have focused on different properties of fuel oxidation over a wide range of conditions, such as ignition delay times in shock tubes [3–8] and rapid compression machines [9–12], species versus time and/or temperature profiles measured in jet-stirred re-

actors [13–17] and flow reactors [18–21], laminar flame speeds [22–26] and spatial distribution of species in flames [27–30]. Moreover, a series of experiments have been performed in engines [31–35] to study homogeneous charge compression ignition (HCCI), engine knock, exhaust gas recirculation (EGR), NO_x emission control, etc. Since 1979 [4] efforts have been made to develop a kinetic model for *n*-heptane oxidation at both low temperature and high temperature to provide further insight into this process. In 1989, Westbrook et al. developed a detailed chemical kinetic mechanism to describe the oxidation of *n*-heptane and iso-octane [36]. This mechanism adopted both low- and high-temperature chemistry, and was validated through comparisons with experimental data from shock tube, turbulent flow reactor and jet-stirred reactors. Later, Chevalier developed a computational technique to automatically develop detailed kinetic mechanisms, which were used to study the influence of fuel, fuel mixtures and fuel additives on

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knock tendency [37]. Ranzi et al. proposed a semi-detailed kinetic model for *n*-heptane oxidation [38], while Côme used a computer package to develop the kinetic models for the oxidation of both *n*-heptane and iso-octane [39].

Curran et al. [40] carried out a comprehensive kinetic modeling study of *n*-heptane oxidation in a systematic way. The important reactions during the oxidation of *n*-heptane were categorized into 25 different reaction classes, including 10 reaction classes to describe high-temperature oxidation and 15 classes to describe the low-temperature regime. Although approximate treatments were assigned to some less important reactions such as the consumption of the heptene isomers, the overall performance of the mechanism was very good. This mechanism has been improved and further validated, with good performance over the pressure range of 3 to 50 atm, in the temperature range of 650 to 1200 K and at equivalence ratios of 0.3 to 2.0. More importantly, this model set a successful frame for the kinetic mechanism development of other larger *n*-alkanes [41]. A more recent study carried out by Mehl et al. [42] on the kinetic modeling of gasoline surrogate components and mixtures under engine conditions has further refined and adopted this mechanism. Moreover, this mechanism also forms the basis for the mechanism development in this work.

There has been a continual interest among the research community in developing a better understanding of *n*-heptane oxidation both experimentally and theoretically. For example, Herbinet et al. performed an experimental study in a jet-stirred reactor [16]. In addition to traditional gas chromatography, the experiments also used synchrotron vacuum ultraviolet photoionization mass spectrometry as the diagnostic technique to identify the unstable species such as radicals, which is an example of the new experimental methods being applied to this kind of study. Herbinet et al. also generated a kinetic mechanism using the software EXGAS [43], which satisfactorily reproduced the mole fraction profiles of most of the species identified in the experiments.

Meanwhile, new reaction pathways are being adopted into the kinetic model to better describe the oxidation process of *n*-heptane. Recently, Pelucchi et al. proposed an improved kinetic model for *n*-heptane [44], by emphasizing new reaction classes producing organic acids, diones and ketones in the low temperature regime. The mechanism was validated over a wide range of conditions including both low and high-temperature ranges. Good agreement was observed between simulations and experimental data from the literature for ignition delay time measurements [5,42,45], species profiles measurements taken in a jet-stirred reactor [14–16] and in a flow reactor [20], as well as laminar flame speeds [26]. Meanwhile, the experimental database of *n*-heptane is being extended to cover a wider range of conditions. Seidel et al. performed an experimental and kinetic modeling study of a fuel-rich, premixed *n*-heptane flame at 40 mbar, and successfully identified over 80 species generated at this condition [30]. Based on previous work, a detailed kinetic model was developed. Reduced kinetic mechanisms are also being proposed, such as the work by Cai and Pitsch [46], who proposed an optimized chemical mechanism for gasoline surrogates which was validated under extensive conditions and it showed a very good performance compared to experimental ignition delay measurements.

This current study is based on a continuity of effort in experimental and kinetic modeling studies of hydrocarbon fuels that we have published previously [47–58]. In this work, the ignition delay times of *n*-heptane in air are firstly measured in two different high-pressure shock tubes to provide more experimental ignition delay time data at elevated pressures. Moreover, the experimental conditions of *n*-heptane oxidation in a jet-stirred reactor have been extended to extremely rich ($\varphi=4.0$) and very lean ($\varphi=0.25$) conditions, while the other conditions remain consistent with those published previously. To reflect the improvements in the chemi-

cal kinetics and thermodynamics as well as their impact, a detailed kinetic model of *n*-heptane oxidation has been developed based on our previous work, including our updated base mechanism [47–50,53,56–58], the sub-mechanisms of the pentane isomers [51,55] and *n*-hexane [54]. In the development of this mechanism, the new reaction classes and reaction rate rules with modifications, which have been successfully applied to the pentane isomers and *n*-hexane, have been adopted. The thermodynamic database has also been updated with recently published optimized group values [52]. The model has been validated using the experimental data sets obtained in this work, as well as those from the literature for ignition delay times, species profile measured in jet-stirred reactors and also for laminar flame speed measurements. Moreover, comparisons are made between the current model and those from recent publications. The significant reaction pathways for the oxidation of *n*-heptane are revealed by further analysis of the simulations.

2. Experimental methods

2.1. PCFC shock tube

The Physico-Chemical Fundamentals of Combustion (PCFC) shock tube at Aachen University has been designed similar to the high-pressure shock tube at NUIG. It has an inner diameter of 63.5 mm and an overall length of about 7.5 m with a 3 m driver section. Due to physical space limitations the driver section is curved with a bending radius of 1 m. The diaphragm section can house up to two pre-scored aluminum diaphragms. All parts coming into contact with fuel/air mixtures are made of stainless steel (316Ti), except for the aluminum diaphragms. Shock velocities and pressure profiles are recorded in the measuring section close to the endwall of the driven section with up to 8 PCB 113B22 pressure sensors. Signals are recorded using a digital oscilloscope with a sampling rate of 25 MHz. Fuel/air mixtures are prepared in a separate 40 L Teflon coated stainless steel mixing vessel. Partial pressures are used to prepare the desired gas mixtures. Static pressures are monitored with two STS ATM. 1st pressure sensors with measuring ranges of 500 mbar and 5 bar, respectively. The shock tube, manifold and mixing vessel can be electrically heated to 150 °C in order to avoid fuel condensation. In this study, initial temperatures of 40 °C are sufficient due to the relatively high vapor pressure of *n*-heptane. Temperatures are monitored with type T thermocouples due to their lower measuring uncertainty compared to conventional type K ones. High purity grade gases for reactive mixture preparation (N_2 and O_2) were provided from Praxair and Westfalia. Helium and compressed air were used as driver gases. The reflected shock conditions were calculated using the initial conditions of pressure and temperature and mixture composition and the measured shock velocity with an in-house code which is based on the shock and detonation toolbox [59] in Cantera [60]. An uncertainty analysis has been performed for the PCFC shock tube and is provided as Supplementary material. Maximum uncertainties in the reflected shock temperatures are estimated to amount to 1.1% in the reflected shock temperature and 3.5% in the reflected shock pressure. Depending on the fuel reactivity this can induce uncertainties of up to 15% in the measured ignition delay time for the range studied.

2.2. NUIG shock tube

High-temperature (above 1000 K) ignition delay times for stoichiometric mixtures of *n*-heptane at compressed pressures of 15 bar in a 21% O_2 : 79% N_2 bath gas were measured in the National University of Ireland, Galway (NUIG) high-pressure shock tube [61], with an inner diameter of 63 mm. The methodology

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