An experimental and modeling study of shock tube and rapid compression machine ignition of *n*-butylbenzene/air mixtures

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ABSTRACT

In our previous work (D. Darcy, C.J. Tobin, K. Yasunaga, J.M. Simmie, J. Würmel, W.K. Metcalfe, T. Niass, S.S. Ahmed, C.K. Westbrook, H.J. Curran, Combust. Flame 159 (2012) 2219–2232), ignition delay times of *n*-butylbenzene in air were measured using a shock tube over a temperature range of 980–1360 K, at reflected shock pressures of 1, 10, and 30 atm, and at equivalence ratios of 0.3, 0.5, 1.0 and 2.0. In the present study, these measurements have been extended to 50 atm and to lower temperatures using a rapid compression machine in the temperature range 730–1020 K, at compressed gas pressures of 10, 30 and 50 atm, over the same equivalence ratio range. Trends in ignition delay times over the wide temperature range were identified. The chemical kinetic model for *n*-butylbenzene, which was validated for the original shock tube data, was extended by adding low-temperature kinetics. The updated chemical kinetic model captures the general trend in reactivity of *n*-butylbenzene over the wide range of temperature, pressure and equivalence ratio conditions studied. Reaction flux analyses were carried out and it was found that fuel H-atom abstraction reactions forming the 4-phenylbut-4-yl radical, and its subsequent addition to molecular oxygen, is the primary source of reactivity in the low-temperature regime. High sensitivity to ignition delay time of the isomerization reactions of alkylperoxy, $\dot{R}O_2 \leftrightharpoons \dot{Q}OOH$, and peroxy-alkylhydroperoxide radicals, $\dot{O}_2QOOH \leftrightharpoons$ carbonylhydroperoxide $+ \dot{O}H$, was also observed at low-temperatures. Comparisons are also made with experimental data obtained for *n*-propylbenzene over the same range of conditions and common trends are highlighted. It was found that, in general, *n*-butylbenzene was faster to ignite over the lower temperature range of 650–1000 K.

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1. Introduction

Alkylbenzenes are one of the major components in diesel fuels [1] and fundamental knowledge of the chemical kinetics of alkyl-benzene fuels is required for further improvement of diesel engines. Carbon numbers for alkylbenzenes in US market diesels for diesel components range in size from approximately C9 to C20 [2,3]. Mueller et al. chose *n*-butylbenzene to be the representative species for alkyl-aromatics in eight-component surrogate mixtures targeting two different diesel fuels [3]. Although diesel fuels contain alkylbenzenes with larger side-chains than *n*-butylbenzene, a study of alkylbenzenes with smaller side-chains, like *n*-butylbenzene, is a necessary first step to develop a fundamental understanding that can be used to develop chemical kinetic mechanisms of larger alkylbenzenes.

There has been extensive previous work on alkylbenzenes. Starting with the small alkylbenzenes, measurements and modeling studies have been performed for ignition delay times for toluene [4–12], ethylbenzene [9–14], xylenes [9,12,14–17] and *n*-propylbenzene [9,10,18–20] at various temperatures and pressures. In the case of *n*-butylbenzene, ignition characteristics as well as flame characteristics have been studied. In early work, Roubaud et al. measured ignition delay times of *n*-butylbenzene using a rapid compression machine in the low-temperature region (600–900 K), at compressed pressures of up to 20 bar, for stoichiometric mixtures of $[O_2]/[inert] = 0.27$ (air) [9] and 0.37 [15], and compared the reactivity of *n*-butylbenzene to similar xylenes. Modeling of the observed low-temperature oxidation of *n*-butylbenzene was conducted by considering an *n*-butane mechanism and taking into account the change of reactivity due to the introduction of the aromatic ring [21].

In our previous work on *n*-butylbenzene, Husson et al. [22] obtained experimental results for its oxidation using three different methods: ignition delay time measurements in a rapid

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compression machine over a temperature range of 640–960 K, at compressed pressures from 13 to 23 bar, and at equivalence ratios of 0.3–0.5; ignition delay time measurements using a shock tube over a temperature range of 980–1740 K, at reflected shock pressures of 1, 10, and 30 atm, for equivalence ratios of 0.3, 0.5, 1.0 and 2.0; species concentration measurements in a jet-stirred reactor over a temperature range of 550–1100 K, at atmospheric pressure, and at equivalence ratios of 0.25, 1.0, and 2.0. They found a large role of the addition to molecular oxygen of resonantly stabilized, 4-phenylbut-4-yl radicals.

n-Butylbenzene has been investigated in other fundamental experimental devices. Diévart and Dagaut [23] studied the diluted oxidation of *n*-butylbenzene using a jet-stirred reactor over the temperature range 550–1150 K at 10 atm for equivalence ratios from 0.25 to 1.5. Won et al. [24] and Ji et al. [25] studied *n*-butyl-benzene extinction limits of counter-flow diffusion flames at atmospheric pressure. Ji et al. also reported laminar flame speeds of *n*-butylbenzene/air mixtures at equivalence ratios from 0.7 to 1.5 and at atmospheric pressure. Pousse et al. [26] studied the high temperature behavior of methane/*n*-butylbenzene/O$_2$/Ar mixtures by measuring temperature and species concentration profiles in a low pressure flat flame at 6.7 kPa, at an equivalence ratio of 0.74, with a ratio of methane/*n*-butylbenzene of 13.5%, and with an oxygen mole fraction of 36.8%. In these studies [24,25], kinetic models of *n*-butylbenzene were extensively validated using the experimental results. However, the temperature, pressure and equivalence ratio conditions of these experiments do not fully cover those experienced in diesel engines, especially at low-temperature, high-pressure, and high equivalence ratio conditions. Experimental results over a wider range of conditions are necessary to develop and validate a chemical reaction mechanism for diesel engines as well as obtaining a fundamental knowledge of the chemical kinetics under these relevant conditions.

The objective of this study is to measure and predict ignition delay times for *n*-butylbenzene/air mixtures over a wide range of temperatures, pressures, and equivalence ratios. Using both a rapid compression machine and a shock tube, the experimental conditions ranged over temperatures of 730–1360 K, pressures of 10, 30, 50 atm, and equivalence ratios of 0.3, 0.5, 1.0 and 2.0. Our previous mechanism which described only high-temperature chemistry has been updated to include the low-temperature reactions in which the fuel radicals add to molecular oxygen and
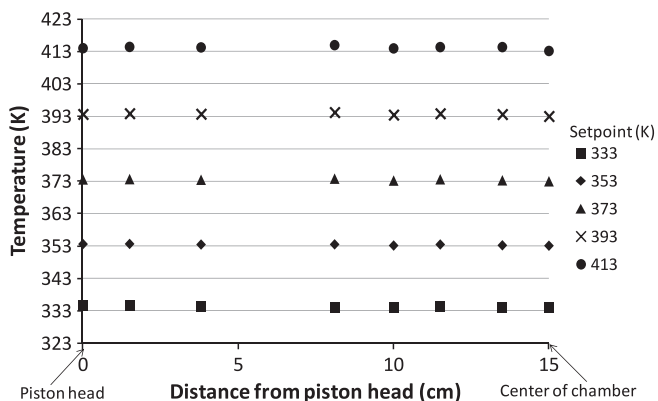

Fig. 2. Temperature profiles inside RCM sleeve and chamber.

proceed to chain branching through a series of isomerization reactions. Measured ignition delay times have been compared with the model predictions and the detailed oxidation of *n*-butylbenzene is described.

2. Experimental

2.1. Rapid compression machine

Ignition delay times at low temperature were measured using a clone of an opposed-piston rapid compression machine originally developed by Affleck and Thomas at Shell-Thornton [27] and re-commissioned at NUIG in the late 1990s [28,29]. Creviced piston heads, with an inner diameter of 38.2 mm, were used in order to improve the post-compression temperature homogeneity in the combustion chamber [30]. The compression ratio was approximately 13:1 in this study. Experimental compression times are relatively short at approximately 16 ms compared to >20 ms in single piston RCM facilities [31,32]. In order to attain the desired pressure and temperature at the end of compression, the initial pressures and temperatures and inert gas compositions (N$_2$, Ar and CO$_2$) were varied. A silicone-coated pressure transducer (Kistler; 603B) was installed in the combustion chamber and pressure traces were recorded using a digital oscilloscope (Pico Technology; PicoScope 4244 PC Oscilloscope). The compressed gas temperature was calculated using Gaseq [33]. Figure 1 shows a typical pressure trace
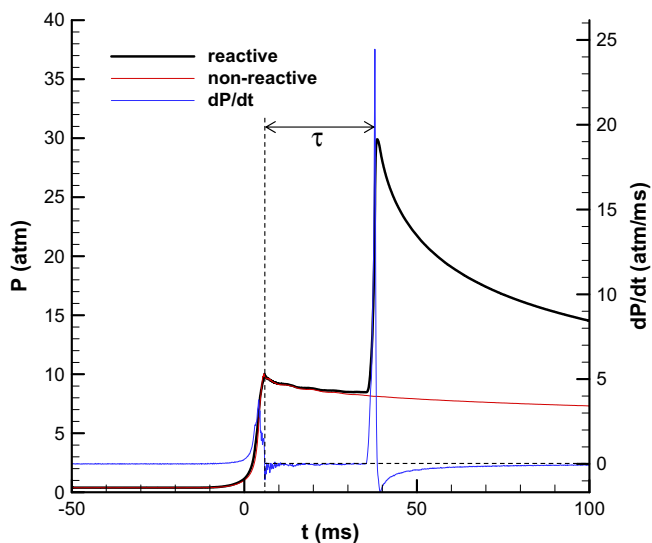

Fig. 1. Typical pressure trace obtained from the NUIG rapid compression machine; $\phi = 1.0$, compressed gas pressure = 10 atm, compressed gas temperature = 893 K.
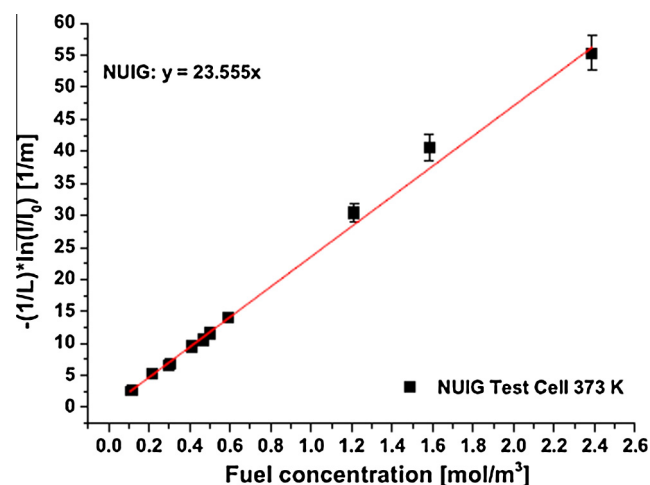

Fig. 3. Evolution of $-(1/L) \cdot \ln(I/I_0)$ as a function of *n*-butylbenzene fuel concentration at 338.15 K.