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ScienceDirect
Proceedings of the Combustion Institute 35 (2015) 341–348
Proceedings of the Combustion Institute
www.elsevier.com/locate/proci

Experimental and modeling study of burning velocities for alkyl aromatic components relevant to diesel fuels

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Abstract

Aromatic species represent a significant fraction (about one third by weight) of both diesel and gasoline fuels. Much of the aromatics in diesel and gasoline are alkyl-benzene species. Although toluene, the lightest of the alkyl-benzenes, has been the subject of extensive literature investigations, very little experimental data are available for heavier alkyl-benzenes (9–20 carbon atoms) relevant to diesel fuel.

In this work, the burning velocity of ethyl-, *n*-propyl- and *n*-butyl-benzenes were measured in a premixed flat-flame burner using the heat flux method. The burning velocities were measured as a function of the equivalence ratio at atmospheric pressure and for two unburned gas temperatures (358 and 398 K). These new experiments are compared with burning velocities for toluene previously measured by the authors. The comparisons showed that ethyl-benzene has the highest flame speed, followed by *n*-propyl- and *n*-butyl-benzenes which have similar burning velocities. Toluene has the lowest flame speed. Excellent agreement was observed between the new measurements and simulations using a mechanism for alkyl-benzenes recently published by Lawrence Livermore National Laboratory (LLNL) and National University of Ireland.

Based on the strong correlation between experiments and calculations, different aspects contributing to the burning speed of the fuels (thermal effects, kinetics, …) were analyzed using the model. A sensitivity analysis was used to determine the reaction rate constants that are most important in determining the flame speed. Reaction path analysis and species profiles in the flame were used to identify the key reaction paths that lead to increase or decrease in the burning velocities. Contrary to what is generally observed for alkanes whose flame speed is controlled by small radical fragments, the flame speed of aromatics is influenced by fuel specific intermediates such as phenyl, benzyl, or even heavier species. The new experimental data and modeling insight generated by this work will support the development of models for heavier alkyl-aromatics of great relevance to diesel fuel.

Keywords: Kinetic modeling; Toluene; Ethyl-benzene; Propyl-benzene; Butyl-benzene

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http://dx.doi.org/10.1016/j.proci.2014.06.064
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1. Introduction

Diesel fuels are complex blends of hundreds of species which include a broad range of hydrocarbons derived from distillation of crude oil and oxygenated molecules used as additives [1,2]. The main classes of molecules found in petroleum-based diesel fuels are *n*- and *iso*-paraffins, naphthenes and aromatic compounds with carbon atom numbers ranging from 10 to 22 (with an average around 14–15) [1]. Each of the three molecular classes comprises about one-third by weight of diesel fuels depending on the origin and treatments of crude oil.

The aromatic fraction of diesel fuels usually consists of single ringed species with one or several side alkyl chains although alkylated double ringed compounds can be found in significant concentrations [2,3]. The study presented in this paper focuses on burning velocities of species representative of the aromatic class of molecules found in diesel fuels: alkyl-benzenes.

Within this class of compounds, *n*-propyl-benzene and *n*-butyl-benzene have received significant attention due to their consideration as surrogate aviation fuel components, as demonstrated by the many experimental and modeling studies [4–9]. Although the boiling point of C_9–C_{10} aromatics falls in the low end of the boiling range of diesel fuels, the chemistry of these components is considered to be archetypical for their class, as indicated by Pitz and Mueller [2] and other studies [10–12].

Laminar burning velocities are important parameters in many areas of combustion science such as the design of burners or engines and for the prediction of explosions. There are limited experimental data in the literature about laminar flame velocities of alkyl-benzenes with more than 8 carbon atoms. Hui et al. studied the oxidation of *n*-propyl-benzene using a twin-flame counterflow setup [4]. Laminar flame velocities of fuel–air mixtures were carried out at atmospheric pressure, at two temperatures (400 and 470 K) and at equivalence ratios ranging from 0.7 to 1.4. The same paper reports the laminar flame velocities of toluene and 1,2,4- and 1,3,5-trimethyl-benzenes at the same conditions for comparison purpose. Ji et al. also measured laminar flame velocities of *n*-propyl-benzene-air mixtures using the counterflow flame configuration [5]. Experiments were performed at atmospheric pressure, at 353 K and over the equivalence ratio 0.7–1.5. They also measured laminar flame velocities of benzene, toluene, the three xylene isomers, and 1,2,4- and 1,3,5-trimethyl-benzenes under the same conditions. These studies revealed that *n*-propyl-benzene laminar flame velocities are lower than that of benzene but faster than that of toluene, xylenes and trimethyl-benzenes. The extensive kinetic analysis presented in Hui and Ji works [4–5] concluded that the flame chemistry of this class of compounds is influenced by the first intermediates formed along the oxidation process of the fuel and, in particular, the formation of resonantly-stabilized benzyl radicals.

In order to supplement the existing set of fundamental data and complement Ji et al. and Hui et al. works [4–5], the burning velocities of increasingly heavy alkyl-benzenes were measured in a premixed flat-flame burner across a wide range of equivalence ratios and temperatures (358–398 K) at atmospheric pressure using the heat flux method. The experimental results were finally analyzed using a recently published detailed kinetic mechanism. This two-fold approach allows to highlight critical aspects dictated by the kinetics of the fuels and to extrapolate information useful to compile detailed mechanisms for this class of compounds.

2. The Experimental apparatus

Measurements of laminar flame velocity were performed using the heat flux method [13] using a flat-flame adiabatic burner which was built following the design proposed by de Goey and coworkers [14–17]. It was recently used to measure laminar flame velocities for components of natural gas [18] and the laminar burning velocity of gasoline fuels with addition of ethanol [19]. The flat flame adiabatic burner used in this study consists of a burner head mounted on a plenum chamber. The burner head is a thin perforated plate made of brass of 30 mm diameter which is used to stabilize the flame. Each small hole of the plate has a 0.5 mm diameter and the pitch between the holes is 0.7 mm. Eight type K thermocouples of 0.5 mm diameter are soldered into the plate surface and are positioned at different distances and angles from the center to the periphery of the burner. The plenum chamber is surrounded by a heating jacket that enables the control of the temperature of the fresh gases (from ambient up to 398 K). The edge of the burner plate is heated at a higher temperature than the one of the fresh gases (about 50 K higher) to keep the temperature of the burner plate constant and to heat up the mixture when it flows through the plate at a higher temperature than the unburned gas mixture. Thus, the heat gain of the unburned gas mixture can compensate for the heat loss necessary for stabilizing the flame. Thermocouple temperature measurements are used to assess the amount of the heat loss or gain. Two thermostatic oil baths provide the heat transfer fluid to the heating and cooling jackets of the burner.

If the gas velocity is lower than the adiabatic flame burning velocity, the sum of the heat loss and heat gain is larger than zero. Then, the center of the burner plate is hotter than the periphery,