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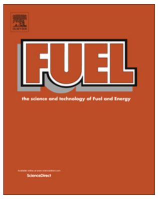

Full Length Article

# Spray ignition experiments for alkylbenzenes and alkylbenzene/n-alkane blends

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## HIGHLIGHTS

- The spray ignition behavior of alkylbenzene/n-alkane blends was investigated.
- A blending model is proposed based on an overall reaction order for each component.
- The nonlinearity of DCN against molar composition is well described by the model.
- Synergism between aromatic ring and alkyl group is seen to enhance reactivity.

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## ABSTRACT

Spray ignition experiments were carried out in a heated constant volume vessel for pure n-octylbenzene and n-decylbenzene and blends of smaller alkylbenzenes (toluene, 1,3,5-trimethylbenzene, n-propylbenzene, and n-butylbenzene) with n-heptane and n-decane. The experiments provide determinations of the derived cetane number (DCN) and the temperature dependence of the spray ignition delay time in air for initial ambient conditions of 650–820 K and 2.14 MPa. The alkylbenzene/n-alkane blends were found to exhibit nonlinear blending for DCN that is well explained using a proposed DCN blending model that accounts for an apparent reaction order of the blend components. Comparisons between n-octylbenzene and n-decylbenzene with blends of smaller n-alkylbenzenes (toluene or n-propylbenzene) and n-alkanes that seek to match functional group distributions, illustrate a synergistic reactivity promotion that occurs for n-alkylbenzenes with long chain alkyl side chain substitutions. This synergism is thought to be result of the weaker benzylic bond strengths within n-alkylbenzenes, providing increased rates of alkyl radical formation and subsequently enhanced low-temperature oxidation. Hence, this finding shows that mixtures of n-alkanes and n-alkylbenzenes with short side chains (e.g., toluene or n-propylbenzene) are not suitable surrogates to emulate low-temperature reactivity of n-alkylbenzenes with long side chains.

## 1. Introduction

Aromatic hydrocarbons are important constituents of all distillate petroleum fuels (diesel, jet, and gasoline), comprising volume fractions of as high as one-third of these fuels [1,2]. They are well known contributors to the formation of particulate matter emissions and are significantly less reactive than paraffinic hydrocarbons, in some cases limiting the overall reactivity of multi-component fuels. Aromatic components act as radical scavengers, reducing the concentrations of important intermediate radical chain carriers (e.g., OH), critical within the chain branching reaction pathways that lead to autoignition [3]. Within the aromatic hydrocarbon family, alkylbenzenes have been extensively investigated in gas-phase experiments, including shock tubes and rapid compression machines [4–10]. Because the carbon range found in jet fuels spans C7–C16 [11], alkylbenzenes with short side chains are clear choices for surrogate fuel components to emulate jet fuel physical and chemical behaviors. As such, mixtures containing alkanes and lighter alkylbenzenes such as toluene, n-propylbenzene, and trimethylbenzene have been considered as surrogate fuel components for jet fuels [12,13]. The alkylbenzene compounds present in diesel fuel have much longer side chains, with carbon numbers spanning C15–C20 [1,14] and are difficult to study in gas-phase experiments owing to their low volatilities. Hence, binary mixtures of n-alkanes and mono-substituted alkylbenzenes with short side chains have been considered as surrogates for large diesel-range alkylbenzene molecules [15–18]. For

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example, Darcy et al. [16] proposed mixtures of n-heptane with n-propylbenzene or n-butylbenzene to mimic the autoignition behavior of n-decylbenzene, although experimental data for n-decylbenzene itself was not available to validate their hypothesis.

Constant volume spray combustion experiments, especially those performed in commercially available devices such as the Ignition Quality Tester (IQT) and Fuel Ignition Tester (FIT), are popular methods for rapid fuel screening. These studies allow for testing fuels with lower volatilities and a wide range of reactivity in the low-temperature combustion regime. The IQT and FIT provide measurements of the Derived Cetane Number (DCN), a fuel reactivity metric, based on an ignition delay determination at a fixed initial thermodynamic condition – for example, 818 K and 2.14 MPa in the IQT test [19]. The DCN is mostly used as a diesel fuel specification [19–21] but it has also been employed as a target property for jet fuel surrogate development [12,13,22]. Naturally, the sensitivities of ignition delay to parameters such as temperature and pressure often need to be considered for both their implications to reaction kinetics and engine applications.

A number of prior studies have reported ignition delay measurements made in constant volume spray combustion experiments for a variety of fuels and fuel components at a range of initial conditions (approximately 650–900 K and 0.1–4 MPa) [23–27]. However, prior studies have mostly either focused on pure fuel components at a range of thermodynamic conditions or on real fuels or multicomponent mixtures at a single thermodynamic state that defines the DCN measurement [12,13,28,29]. Furthermore, in multicomponent mixtures, ignition can be influenced by nonlinear mixing rules for chemical reactivity (e.g., ignition delay and cetane and octane numbers) [30–33] and can sometimes be complicated by physical effects such as preferential vaporization [34] leading to local non-uniform fuel mixtures where ignition occurs [35].

The present study is motivated by an interest in the influence of the aromatic contribution to autoignition properties of surrogate mixtures and fuels containing aromatics. We report ignition delay data for binary mixtures of n-alkanes and alkylbenzenes and for pure n-alkylbenzenes containing long side chains. The objectives of the study are: (1) to deduce the influence of the aromatic function on the overall reactivity of fuel sprays; (2) determine the temperature dependence of spray ignition delay times for alkylbenzene/n-alkane mixtures; (3) characterize the spray ignition delay for two large n-alkylbenzenes characteristic of those found in diesel fuels, n-octylbenzene and n-decylbenzene, and compare those results to those for mixtures of n-alkanes and smaller n-alkylbenzenes, which may be suitable simplifying surrogates in both experiments and modeling; and (4) consider rules for the experimentally observed nonlinear blending for reactivity.

## 2. Experimental method

Spray ignition experiments were performed in a constant volume spray combustion chamber (CVSCC) whose features and operating procedure has been detailed in a previous study on pure normal, branched, and cyclic alkane spray ignition [27]; see Fig. 1 for a schematic of the CVSCC. One conclusion of the prior work on alkanes is that for moderate to high reactivity fuels, the reactivity trends in the CVSCC are the same as displayed in the commercial IQT and FIT devices used to measure DCN; hence, ignition delay results from the CVSCC can be correlated against known DCNs to provide DCN determinations.

In the CVSCC, a fuel spray is injected (injection pressure of 15.2 MPa, FI01 in Fig. 1) into a combustion chamber with a volume of 0.5 L (length = 11 cm and diameter = 7.6 cm). The spray duration can be varied from 4 to 15 ms and is controlled to within ±0.5 ms of the targeted duration. For all experiments reported in this paper, the targeted spray duration was 7 ms, a value chosen such that it provided repeatable injections for the range of fuels considered. The CVSCC is pressurized with medical grade air (21% $O_2$) and pre-heated to a desired initial ambient temperature prior to spray injection. The pressure and temperature prior to spray injection are recorded using a static pressure gauge and type-K thermocouple. To achieve fuel injection, a square-wave electronic pulse is supplied to a solenoid valve which provides fuel pressure to the mechanical pintle-style injector. The start of injection (SOI) and duration of injection are determined from dynamic pressure measurements made in the fuel line at the injector with uncertainty in both SOI and injection duration of ±0.1 ms [27]. SOI is defined using the local maximum in the rate of injection pressure rise immediately before the injection pressure itself reaches a maximum [27]. The time history of the CVSCC pressure was measured using a water-cooled pressure transducer (PR01 in Fig. 1) mounted in the chamber wall facing the fuel injector and allows for determination of the start of combustion (SOC), used for defining the spray ignition delay. Example signals for the fuel line pressure and chamber pressure are illustrated in Fig. 2.

Consistent with the definition used in our work on alkanes [27], the ignition delay time, $\tau$, is defined as SOC – SOI, where SOC is defined as the time at which the rate of heat release (RHR) achieves its maximum value. The time history of RHR is determined from the dynamic chamber pressure using a simple thermodynamic relationship (equation 1) for a constant volume, adiabatic vessel, where $Q$ is the heat release, $P$ is the chamber pressure, $V_0$ is the volume of the chamber (500 mL), and $\gamma$ is the specific heat ratio which here is taken to be a constant 1.35. The choice of $\gamma$ is not important, as the RHR is used to determine the ignition delay based on its temporal evolution and RHR is not considered in a quantitative sense.

$$RHR = \frac{dQ}{dt} = \frac{V_0}{\gamma - 1}\frac{dP}{dt} \tag{1}$$

In our previous work [27], ignition delay time measurements were reported from single shot experiments performed across a range of highly-sampled temperatures with selected conditions repeated. Here, given the simple temperature dependence previously observed for alkanes and also observed for the present fuels, multiple ignition delay measurements were carried out at a sparser range of common ambient temperatures and are reported as the average ignition delay for a given temperature, where between five and fifteen experiments were carried out for each condition. The number of experiments performed depended upon the duration of the measured ignition delay and initial ambient temperature, such that the standard deviation in ignition delay was less than ±5%.

The uncertainty in the determination of the SOI is itself accurate to ±0.1 ms and hence the deviation in ignition delay determinations converges to slightly greater than ±0.1 ms for short ignition delay times (higher temperatures). Uncertainty in the ambient temperature dominates for longer ignition delay times (lower temperatures), where ignition delay is more sensitive to temperature within the temperature range considered. In the example exhibited in Fig. 2, the spray ignition of an equimolar blend of n-propylbenzene and n-decane, the measured ignition delay is 4.71 ± 0.15 ms for seven consecutive experiments with injection duration of 6.8 ± 0.1 ms, temperature of 818.3 ± 0.7 K, and pressure 2.14 ± 0.02 MPa.

### 2.1. Fuels

Spray ignition delay times for binary blends of alkylbenzenes and n-alkanes and two large n-alkylbenzenes are reported. The