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Experimental and Modeling Study of Laminar Flame Speeds for Alkyl Aromatic Components Relevant to Diesel Fuels

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Real fuels are complex blends of hundreds of hydrocarbon species derived from the distillation and processing of crude oil. Aromatic species represent a significant fraction (about one third by weight) of both diesel and gasoline fuels. Therefore, experimental and modeling studies are needed to understand the combustion process of this chemical class. 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) that are present in diesel fuel.

In this work, laminar flame speeds of ethyl-, *n*-propyl- and *n*-butyl-benzenes were measured in a premixed flat-flame burner using the heat flux method. The flame speeds were measured as a function of the equivalence ratio at atmospheric pressure and at three unburned gas temperatures (298, 358 and 398 K). These experimental data are compared with flame speeds 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 flame speeds. Toluene has the lowest flame speed. The experimental data obtained with the heat flux method was compared with literature data using other methods. The new experimental data agreed with the literature data, except for the case of *n*-propyl-benzene.

The experimental results have been analyzed using a detailed kinetic mechanism recently developed at LLNL for this class of compounds. In general, modeling and experimental results agreed very well. The detailed chemical kinetic model has been used to determine the key factors controlling the flame speeds of the fuels. Using Chemkin Pro®, 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 and decrease the flame speeds. Contrary to what is generally observed for alkanes whose flame speed is controlled by small radical fragments, the flame speed of aromatics can be influenced by fuel specific intermediates such as phenyl, benzyl, or even heavier species. The reactive radicals produced by the breaking of the weak benzylic C-C bond in these alkyl-benzenes compared to the intrinsic stability of the benzyl-type radicals produced by this bond rupture leads to the formation of reactive and unreactive radical pools whose relative amounts control the flame speed. The new knowledge derived from our study of these four alkyl-benzenes will be used in future work to develop models for heavier alkyl-aromatics of greater relevance to diesel fuel.

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 according to 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 also be found [2]. The study presented in this paper focuses on laminar flame velocities of species representative of the aromatic class of molecules found in diesel fuels: alkyl-benzenes.

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 very little experimental data in the literature about laminar flame velocities of alkyl-benzenes with more than 8 carbon atoms. Table 1 summarizes the existing experimental studies on n-propyl-benzene. Hui et al. studied the oxidation of *n*-propyl-benzene using a twin-flame counterflow setup [3]. 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 [4]. 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.

Species	**Method**[a]	**T_u (K)**[b]	**P (bar)**	**φ**	**References**
n-propyl-benzene	CFF	353	1	0.7 – 1.5	[4]
		400, 470	1	0.7 – 1.4	[3]

[a] CFF: counter-flow flame.

[b] The unburned gas temperature.

Table 1*: Experimental studies reporting laminar flame velocities of n-propyl-benzenes– air flames.*

2. The Experimental Apparatus

Measurements of laminar flame velocity were performed using the heat flux method [8] using a flat-flame adiabatic burner which was built following the design proposed by de Goey and coworkers [9–12]. It was recently used to measure laminar flame velocities for components of natural gas [13] and the laminar burning velocity of gasoline fuels with addition of ethanol [14].

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 water 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, and the flame is stabilized under subadiabatic conditions. On the other hand, if the unburned gas velocity is larger than the adiabatic burning velocity, the center of the burner plate is cooler than the periphery and the flame is stabilized under superadiabatic conditions. Thus, when the burner head temperature profile is flat, it means that no heat is lost or gained by the flame so that the flame becomes adiabatic. By changing the flow rate of the gas mixture, it is also possible to find an appropriate value of the gas velocity to cancel out the net heat flux so that the radial temperature distribution in the burner plate is uniform and equal to the temperature of the heating jacket. The flow rate at which the net heat flux is zero corresponds to the adiabatic flame burning velocity.

Gas flow rates were controlled using Bronkhorst High-Tech Mass Flow Controllers. Oxygen and nitrogen were delivered by Messer. The purity of these two gases was 99.995%. For liquid fuels, flow rates were measured using a Bronkhorst mini-CORI-FLOW Mass Flow Controller coupled to an evaporator. Ethyl-benzene (≥99%) and *n*-propyl-benzene (≥98%) were provided by Sigma-Aldrich. As the adiabatic laminar burning velocity is found when the net heat loss is zero, the error is only dependent on a few factors. The error in the laminar burning velocity can be attributed to the error in the mass flow measurements (around 0.5% for each MFC) which can lead to a global error of 1.5% in the laminar flame velocity, the error in the reading of the temperature with thermocouples which could lead to an error of around 0.2 cm/s in the laminar flame velocity, and to errors due directly to flame distortions, such as edge effects for example (around 0.2 cm/s). Concerning the determination of equivalence ratios, note that the main error is due to the error in the mass flow measurements which leads to an error of about 1%. Finally, there are some qualitative errors which are difficult to evaluate such as the possible errors in the fresh gas temperature if the gaseous mixture does not spend enough time in the plenum chamber to uniformly reach the temperature of 298 K. Possible errors in the fuel purity are minute since high purity gases are used.

3. Experimental Results

The apparatus here described was used to measure laminar flame velocities of various aromatic compounds (at ambient condition) relevant to gasoline and diesel fuels. Experiments were performed at atmospheric pressure, at different fresh gas temperatures in the range 298-398 K, and using synthetic air (79% (vol) nitrogen and 21% (vol) oxygen). Data obtained in this study were systematically compared with data from the literature when available.

Laminar flame velocities have been measured for three alkyl-benzenes: ethyl-, *n*-propyl- and *n*-butyl-benzenes. The range of conditions at which measurements were possible (temperature, equivalence ratio) was narrowed due to the low vapor pressure of these types of hydrocarbons. As an example, laminar flame velocities of ethyl-benzene and heavier species could not be acquired at 298 K.

Figure 1 to Figure 3 display the laminar flame velocities obtained in this study for the three alkyl-benzenes: ethyl-benzene, *n*-propyl-benzene and *n*-butyl-benzene. Vapor pressures of alkyl-benzenes are relatively low and laminar flame velocities could only be measured at 358 and 398 K over limited ranges of equivalence ratios.

Data obtained for *n*-propyl-benzene in this study were compared with data from Ji et al. at 353 K [4] and Hui et al. at 400 K [3] in the counterflow configuration (). Data from Ji et al. are in good agreement with data obtained in this study at equivalence ratios below 0.8. Above 0.8, laminar flame velocities from Ji et al. are slower than our data (by more than 2 $cm\cdot s^{-1}$). Data published by Hui et al. at 400 K strongly disagree with our data obtained at 398 K: their laminar flame velocities are faster, especially at equivalence ratios less than 1.1 (the gap reaches 8 $cm\cdot s^{-1}$). The observed discrepancies between the different sets of data suggest that further experimental studies are needed to confirm the values of laminar flame velocities for *n*-propyl-benzene.

The laminar flame speeds measured for n-butyl benzene are shown in Fig. 3 over the range of equivalence ratios that could be achieved in the experimental facility. The peak in flame speed occurs at an equivalence ratio of approximately 1.05. The flame speed increases when the unburned gas temperature is raised. Again, the agreement between the experimental and simulated results is excellent.

Figure 4 displays the comparison of experimentally-measured laminar-flame velocities of alkyl-benzenes from toluene up to *n*-butyl-benzene at 358 K using the author’s facility. Toluene data used in this comparison are from a previous study [14].

It can be seen that laminar flame velocities of ethyl-, *n*-propyl- and *n*-butyl-benzenes are relatively similar and that laminar flame velocities of toluene are slower than the ones of the three other species at equivalence ratios larger than 0.9. Ethyl-benzene appears to be the fuel having the fastest flame speed. It is observed that the gap between laminar flame velocities of toluene and the ones the three other species gets smaller at 358 K.

4. The LLNL alkyl aromatics’ kinetic mechanism

Laminar flame velocities for the three alkyl-benzenes were computed using a detailed kinetic developed at LLNL for this class of compounds. This mechanism is based on a newly published C0-C4 mechanism developed at NUI Galway (Aramco 3.14) which has been extensively validated on a wide range of experimental data including ignition delay times, laminar flame speeds and flow reactor speciation [16]. The base chemistry was complemented by a toluene mechanism derived from Metcalfe et al. [17]. The original mechanism by Metcalfe et al. has been revisited with particular attention to the cyclopentadienyl chemistry. The addition of the C_5H_5 radical on C_5H_6 and the recombination of cyclopentadienyl radicals to form larger aromatic species were modified and new rates from Cavallotti et al. [18] were adopted. In order to achieve a satisfactory agreement with the flow reactor data presented in the experimental study by Buttler and Glassman [19] the recommended reaction rates proposed by Cavallotti had to be multiplied by a factor 2. This coupled model constitutes the extended base chemistry for aromatics currently in use by NUI and LLNL.

The extended base chemistry has been merged with the alkyl-benzene mechanisms discussed by Darcy et al. [20] and later revised in [21]. The butyl-benzene mechanism was updated with the same reaction rate rules used for propyl-benzene [21]: abstraction reaction rate constants for the secondary benzyl hydrogen by the major radical species (e.g. H·, OH·, O·, CH_3·, HO_2·, …) and O_2 were assigned to match the rates adopted for olefinic systems for abstraction reactions involving secondary allylic hydrogens [22]. Similarly, abstraction reaction rates on secondary and primary radicals were assumed to be the same as used for alkane species. Rate constants for beta-decomposition reactions of alkyl-benzene radicals were specified in the exothermic direction which represents the addition of a radical to an alkene moiety.

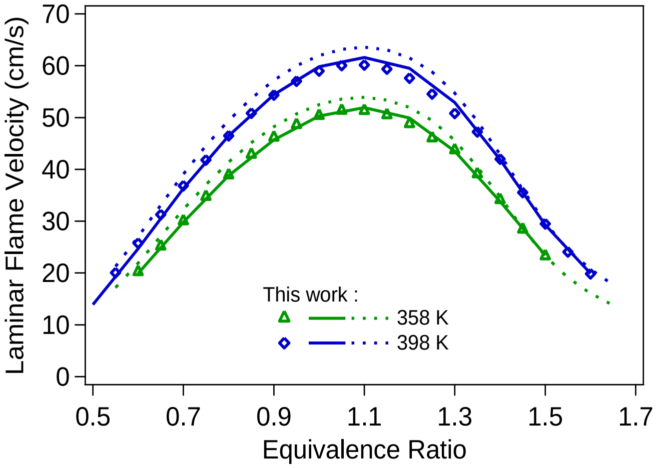

Figure 1*: Laminar flame velocities as a function of equivalence ratio for ethyl-benzene at two fresh gas temperatures (358 – 398 K). Symbols are experimental data and lines simulations (solid line: LLNL model; dotted line: model from the literature [15]).*

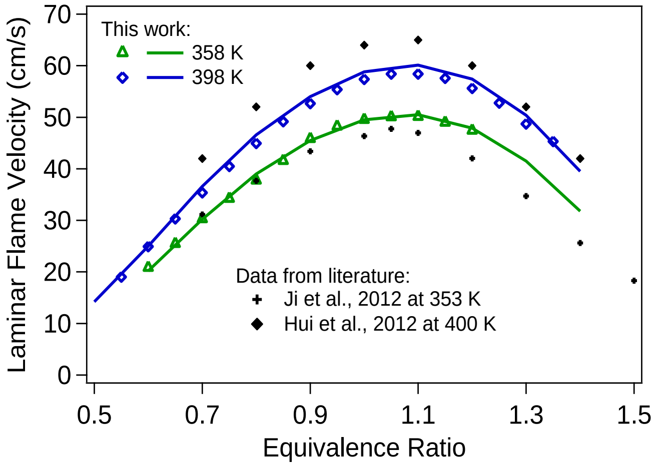

Figure 2: *Laminar flame velocities as a function of equivalence ratio for n-propyl-benzene at two fresh gas temperatures (358 and 398 K). Symbols are experimental data and lines simulations performed using the LLNL model. Comparisons with experimental data from Hui et al. [3] and Ji et al. [4].*

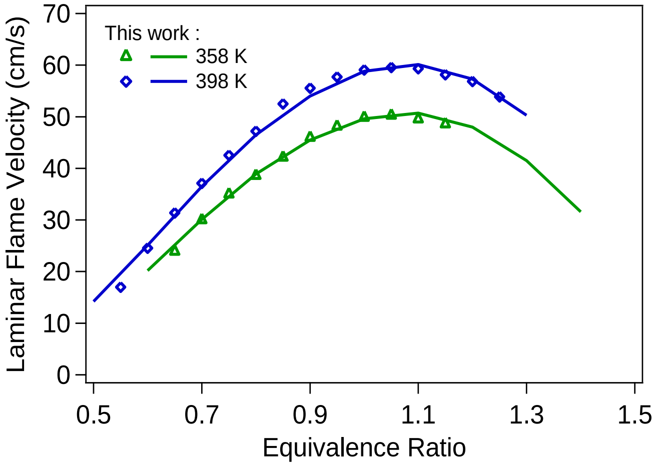

Figure 3: *Laminar flame velocities as a function of equivalence ratio for n-butyl-benzene at two fresh gas temperatures (358 and 398 K). Symbols are experimental data and lines simulations LLNL model.*

Finally, the reaction pathways describing the oxidation of polyaromatic species are derived from Narayanaswamy et al. [23].

The thermodynamic data for the *n*-propyl-benzene species were the same as in [21]. The resulting mechanism includes about 500 species and 2600 reactions.

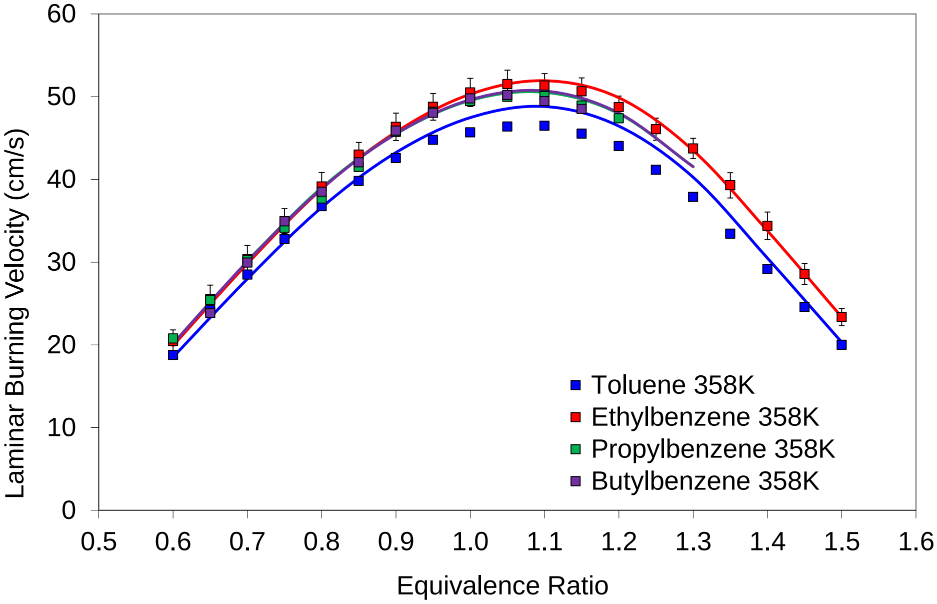

Figure 4: *Comparison of laminar flame velocities (Symbols: Experiments, Lines: Calculations) as a function of equivalence ratio for alkyl-benzenes from toluene up to n-butyl-benzene at 358 K. Toluene data are from a previous study [14].*

5. Kinetic analysis

Before simulating the present experiments, alkyl-benzene mechanism was validated by comparing computed results to experimental ignition delay times from shock tubes and rapid compression machines. Speciation measurement from flow reactors and stirred reactors were also used to validate the mechanism. Good agreement was obtained for these comparisons. After these mechanism validations, the detailed kinetic model by LLNL was used to investigate the trends in the flame speed rates highlighted in the present experiments. The modeling results followed the trends identified in the experiments (Fig. 4): ethyl-benzene has the highest flame speed, followed by *n*-propyl- and *n*-butyl-benzenes which have similar flame speeds. Toluene has the lowest flame speed. Results from the chemical kinetic model also showed excellent quantitative agreement (within 1.5 cm/s) with the experimental data for n-ethyl, n-propyl and n-butyl-benzene (Figs. 1-3).

Based on these encouraging results, the detailed chemical kinetic model has been used to determine the key factors controlling the flame speeds of alkyl-benzenes. Using Chemkin Pro®, an A-factor sensitivity analysis was performed at Φ=1.2 and T_u=358K for toluene, ethyl-benzene and *n*-propyl-benzene and the reaction rate constants that are most important in determining the flame speed of the three fuels were identified. Due to the similarity between *n*-propyl-benzene and *n*-butyl-benzene, we assumed that the chemistry controlling the flame speed of the two species will be analogous. Reaction path analysis was used to identify the key reaction paths that lead to increase and decrease the flame speeds. Species profiles for some relevant species were also analyzed. Contrary to what is generally observed for alkanes whose flame speed is controlled only by small radical fragments, the flame speed of aromatics were found to be influenced by fuel specific intermediates such as phenyl, benzyl, or even heavier species. The intrinsic stability of the resonantly stabilized benzyl structures, compared with the weakness of the side chain, leads to the formation of unreactive and reactive radical pools whose relative amounts control the flame speed.

In order to better identify on the differences among the three alkyl aromatics, only the reactions having the highest sensitivity coefficients (>0.01) and a difference of more than 30% within the maximum and minimum sensitivity across the three fuels were considered in our analysis. The resulting plot is shown in figure 5.

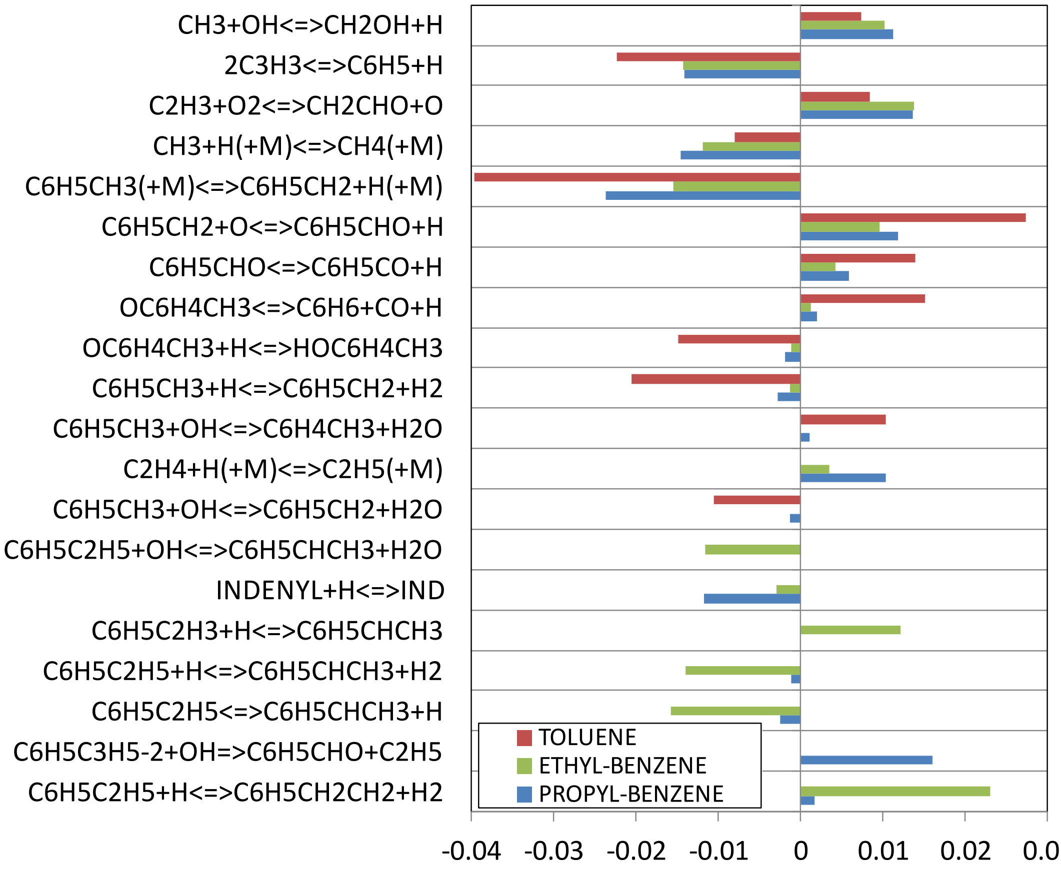

Figure 5*- A-Factor sensitivity analysis laminar flame speed of toluene, ethyl-benzene and n-propyl-benzene at* Φ=1.2 and T_u=358K. *Only the reactions having a sensitivity coefficients >0.01 and a difference of more than 30% within the maximum and minimum sensitivity across the three fuels are shown. Positive sensitivity indicates that an increase in the reaction rate constant for the specified reaction increases the flame speed.*

From the sensitivity analysis it is clear that the formation of resonantly stabilized radicals (e.g. benzyl radicals, cresoxy radicals…) is a key element controlling the flame speed of aromatic species. These radicals reach high concentrations in the region right before the flame front, scavenging the H·radicals responsible for the high temperature branching reaction. Of particular interest is $C_6H_5CH_3 = C_6H_5CH_2 + H$ which shows the highest sensitivity. The flame speed is sensitive to the reverse direction of this reaction: the recombination of H and with the $C_6H_5CH_2\cdot$ radical. That the reverse direction was important was confirmed with reaction path analysis presented below.

The importance of the benzyl radical was confirmed by examining how the peak concentration of the $C_6H_5CH_2\cdot$ radical varies among the three fuels (Fig. 6): toluene produces the highest concentration of benzyl radicals, followed by *n*-propyl-benzene and ethyl-benzene, which shows the lowest peak. This trend is the opposite of that observed for the flame speeds of the three fuels. A reaction flux analysis showed in Figure 7 helped identifying the major reaction pathways leading to the formation of benzyl radicals. H abstractions are the main pathways leading to the resonantly stabilized $C_6H_5CH_2\cdot$ in the toluene flame, while the homolytic cleavage of the benzylic C-C bond dominates in the ethyl- and *n*-propyl-benzene flames. Abstraction reactions are much faster at low temperature than the initiation reactions, making the $C_6H_5CH_2\cdot$ formation possible for toluene in a broader range of the pre-flame region. On the other hand, the other alkyl-benzenes have a weak benzylic C-C bond which toluene lacks. This bond breaks much faster than reaction with H atoms can occur in these flames. One major effect of the presence of high concentration of benzyl radicals in toluene flames is that they effectively quench the reactivity zone neutralizing the H· radicals that back diffuse from the flame region. These results are consistent with what previous found by Ji et al [4] who highlighted the production of benzyl radicals followed by the recombination of $C_6H_5CH_2 + H$ as the key step controlling the relative flame speed of toluene (slower) and propyl-benzene (faster).

Other reactions of some importance are the abstraction on the alkyl chain of ethyl-benzene. Depending on the selectivity of the abstraction on the primary or secondary carbon the resulting radical intermediate can be a stable secondary benzyl radical, which decreases the reactivity of the system, or a fast propagating $C_6H_5CH_2CH_2\cdot$ radical, which readily decomposes to styrene and H. Small radicals also affect the flame propagation process with methyl radicals leading to termination reactions and ethyl radicals to H· formation.

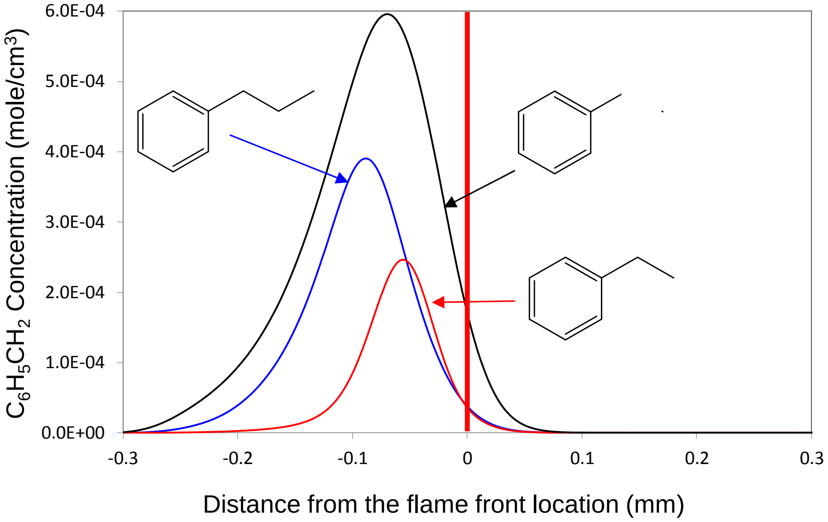

Figure 6- *Calculated concentration profiles of the benzyl radicals at* $\Phi=1.2$ *and* $T_u=358K$ *for toluene, ethyl-benzene and n-propyl-benzene along the axial coordinate. The red vertical line indicates the location of the flame front.*

6. Conclusions

Laminar flame velocities for several components belonging to the aromatic class of hydrocarbons found in diesel fuels were measured using the heat flux method (e.g. ethyl-, *n*-propyl- and *n*-butyl-benzenes). Experimental data obtained in this study were compared with literature data. Unfortunately there are very little data available for comparison (laminar flame velocities were available for *n*-propyl-benzenes). Discrepancies between the newly measured data and the existing literature data were highlighted. New measurements obtained with different types of methods are necessary to confirm the values of laminar flame velocities of these fuels.

Comparisons of experimental data obtained in this study showed that there are very little differences in the laminar flame velocities of alkyl-benzenes larger than ethyl-benzenes and some interesting trends among alkyl aromatics having different side chain lengths were observed.

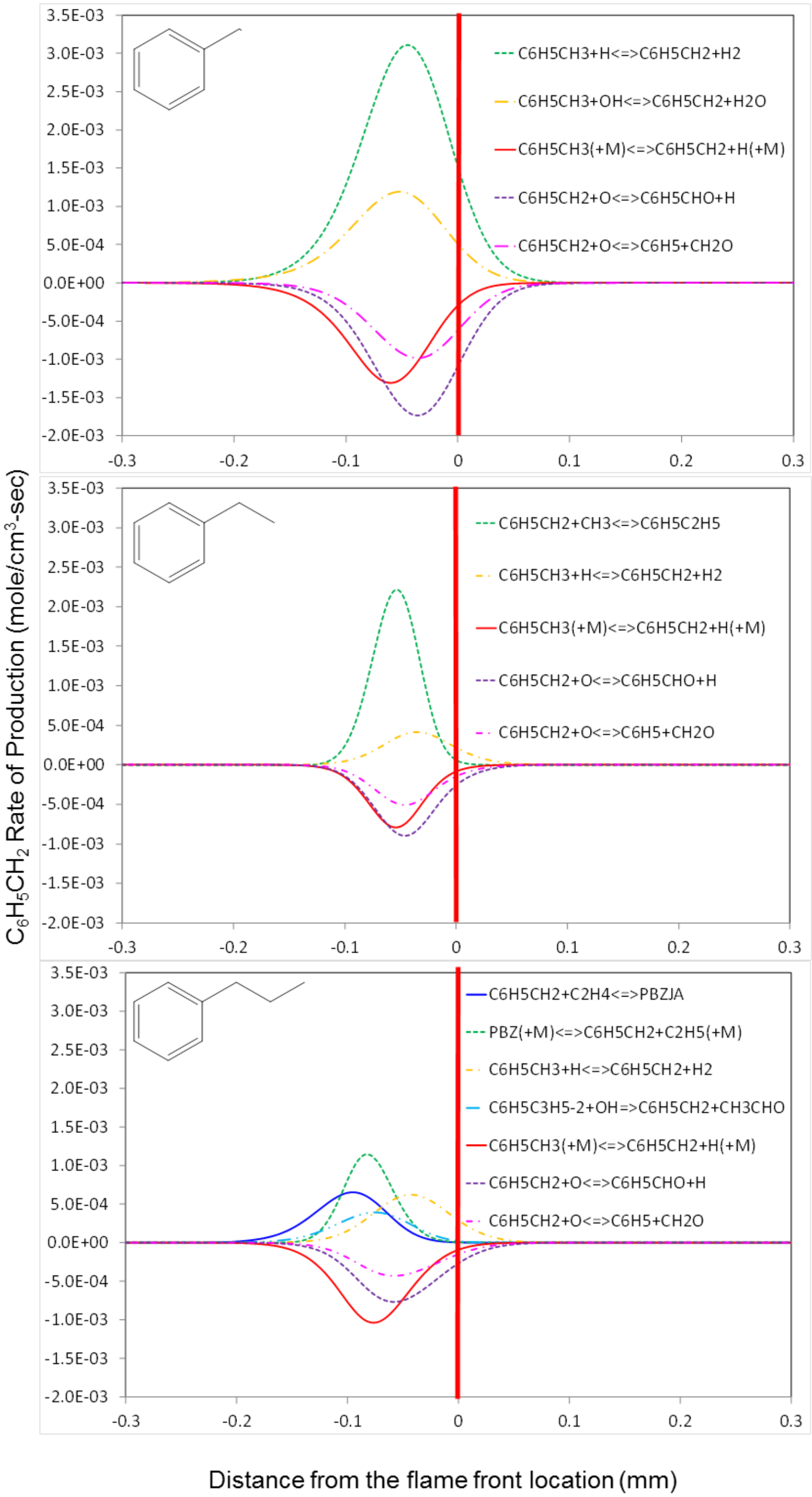

Figure 7 - *Calculated rate of production of the benzyl radicals at* Φ=1.2 *and* T_u=358K *along the axial coordinate of the flame for toluene, ethyl-benzene and n-propyl-benzene. The red vertical line indicates the location of the flame front.*

Experimental data were compared with data computed using detailed chemical kinetic models. Predictions obtained with the kinetic model for alkyl-benzenes developed at LLNL were in very good agreement with experimental data measured in this study and the trends highlighted in the experiments were reproduced by the model.
The kinetic mechanism was used to analyze the chemistry controlling the flame speed. Sensitivity analysis and reaction path analysis were performed and species concentrations were computed. These numerical results showed that the chemistry of the resonantly stabilized radicals (in particular the benzyl radicals) is responsible for the differences in flame speeds observed among toluene, ethyl-benzene and *n*-propyl-benzene. Toluene resulted to be a much more effective source of resonantly stabilized radicals compared to the other two fuels. While ethyl- and *n*-propyl-benzene produce benzyl radicals primarily via initiation reactions, toluene's slow initiation reactions allow weak benzylic hydrogens to be abstracted by the radicals that are back diffusing from the flame region. The resulting high concentration of benzyl radicals scavenges H radicals via termination reactions, inhibiting the flame propagation.

Acknowledgements

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References

[1] J.T. Farrell, N.P. Cernansky, F.L. Dryer, C.K. Law, D.G. Friend, C.A. Hergart, R.M. McDavid, A.K. Patel, C.J. Mueller, H. Pitsch, Development of an Experimental Database and Kinetic Models for Surrogate Diesel Fuels, SAE International, Warrendale, PA, 2007.

[2] W.J. Pitz, C.J. Mueller, Progress in Energy and Combustion Science 37 (2011) 330‐350.

[3] X. Hui, A.K. Das, K. Kumar, C.-J. Sung, S. Dooley, F.L. Dryer, Fuel 97 (2012) 695‐702.

[4] C. Ji, E. Dames, H. Wang, F.N. Egolfopoulos, Combustion and Flame 159 (2012) 1070‐1081.

[5] C. Ji, E. Dames, B. Sirjean, H. Wang, F.N. Egolfopoulos, Proceedings of the Combustion Institute 33 (2011) 971‐978.

[6] F. Wu, A.P. Kelley, C.K. Law, Combustion and Flame 159 (2012) 1417‐1425.

[7] T. Dubois, N. Chaumeix, C.-E. Paillard, Energy Fuels 23 (2009) 2453‐2466.

[8] L.H.P. De Goey, A. Van Maaren, R.M. Quax, Combust. Sci. Technol. 92 (1993) 201‐207.

[9] A. Van Maaren, D.S. Thung, L.H.P. De Goey, Combust. Sci. Technol. 96 (1994) 327‐344.

[10] I.V. Dyakov, A.A. Konnov, J. De Ruyck, K.J. Bosschaart, E.C.M. Brock, L.P.H. De Goey, Combust. Sci. Technol. 172 (2001) 81‐96.

[11] A.A. Konnov, I.V. Dyakov, J. De Ruyck, Exp. Therm. Fluid Sci. 27 (2003) 379‐384.

[12] K.J. Bosschaart, L.P.H. De Goey, Combust. Sci. Technol. 176 (2004) 1537‐1564.

[13] P. Dirrenberger, H. Le Gall, R. Bounaceur, O. Herbinet, P.-A. Glaude, A. Konnov, F. Battin-Leclerc, Energ. Fuel. 25 (2011) 3875‐3884.

[14] P. Dirrenberger; P-A. Glaude; R. Bounaceur; H. Le Gall; A. Pires da Cruz; A. Konnov; F. Battin-Leclerc, Submitted to Fuel

[15] B. Husson, M. Ferrari, O. Herbinet, S.S. Ahmed, P.-A. Glaude, F. Battin-Leclerc, Proceedings of the Combustion Institute 34 (2013) 325‐333.

[16] H.J Curran., W.K. Metcalfe, S. Burke ,S. Ahmed , "A Hierarchical and Comparative Kinetic Modeling Study of C1-C2 Hydrocarbon and Oxygenated Fuels", Submitted

[17] W.K Metcalfe., S. Dooley, F.L Dryer., Energy and Fuels, 25, 11, 4915–4936 (2011)

[18] C. Cavallotti, D. Polino, A. Frassoldati, E. Ranzi, J Phys Chem A. 2012 Apr 5;116(13):3313-24.

[19] R. G. Butler , I. Glassman, Proc. Combust. Inst 32 (2009) 395–402

[20] D. Darcy, C.J. Tobin, K. Yasunaga, J. M. Simmie, J. Wurmel, W.K. Metcalfe, T. Niass, S.S. Ahmed, C.K. Westbrook, H.J. Curran, Combustion and Flame 159 (2012) 2219–2232

[21] Darcy D., Mehl M., Simmie J.M., Würmel J., Metcalfe W.K., Westbrook C.K., Pitz W.J., Curran H.J., Proc. Combust. Inst, Volume 34, Issue 1, 2013, Pages 411–418

[22] M. Mehl, W.J. Pitz, C.K. Westbrook, K. Yasunaga, C. Conroy, H.J. Curran, Volume 33, Issue 1, 2011, Pages 201–208
[23] K. Narayanaswamy, G. Blanquart, H. Pitsch, Comb. Flame, 157 (2010) 1879-1898