Laminar burning velocity of gasoline and the gasoline surrogate components iso-octane, n-heptane and toluene

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HIGHLIGHTS

- The laminar burning velocity has been measured for gasoline and surrogate components.
- A toluene reference fuel reproduced the laminar burning velocity of gasoline.
- The temperature dependence of the laminar burning velocity is shown.
- The temperature dependence has a minimum around peak burning velocity.

ARTICLE INFO

ABSTRACT

Laminar burning velocities have been measured using the heat flux method on a flat flame adiabatic burner. Measurements were done for iso-octane, n-heptane, toluene, a toluene reference fuel (i.e., a mixture of iso-octane, n-heptane and toluene) and a commercial gasoline. The laminar burning velocities of the toluene reference fuel were in correspondence with the laminar burning velocities of the commercial gasoline. Measurements were done for an equivalence ratio from 0.7 to 1.3 and for a range of temperatures between 298 K and 358 K. The temperature dependence of the fuels is shown and the measurements are compared to literature data and simulations using reduced kinetic models.

1. Introduction

The laminar burning velocity (u_l) is a physicochemical property dependent on the temperature, pressure, and mixture composition (fuel type, equivalence ratio, and amount of diluents). As a result, the laminar burning velocity provides invaluable information on the combustion properties and the underlying oxidation chemistry of the given fuel. It is also an important parameter in the design of engines, burners and other equipment where combustion is involved. Several experimental setups can be used to measure the laminar burning velocity of fuels: flat flame burners, combustion chambers, counterflow burners, etc. [1]. However, experimental measurements of the laminar burning velocity are mostly limited in pressure and temperature and can be compromised by the effects of flame stretch and instabilities. Computationally, these effects can be avoided by calculating one-dimensional, planar adiabatic flames using chemical oxidation mechanisms. The velocity of these flames is the laminar burning velocity by definition. Thus kinetic models can be used to calculate the laminar burning velocity over a range of conditions used in practical applications. Computer simulations where combustion chemistry is involved, e.g. CFD study of an internal combustion engine, are computationally demanding. As a result, to calculate the laminar burning velocities, they rely in many cases on reduced kinetic models or correlations which give the laminar burning velocity in terms of pressure, temperature and composition of the unburned mixture, to have faster computation times. These reduced kinetic models and correlations should predict the correct temperature, pressure and diluents dependence.

For gasoline, it is currently not possible to represent the complex chemistry in a chemical kinetic model [2]. Because of the complexity of gasoline and because of the varying composition of gasoline, gasoline surrogates are used in experiments and in calculations. The term surrogate gasoline refers to a simpler representation of a fully-blended fuel [2]. The most common gasoline surrogates are iso-octane or binary mixtures of iso-octane and n-heptane, the primary reference fuels (PRF's) for determining octane

ratings for spark ignition engine fuels. Several studies concerned the laminar burning velocity of iso-octane, n-heptane and mixtures of these two fuels [3–12].

Jerzembeck et al. [10] compared the laminar burning velocity of a commercial gasoline and a PRF mixture with a research octane number of 87. The agreement was very good for lean mixtures but deviations were found for rich and stoichiometric mixtures. Stanglmaier et al. [13] reported that the laminar burning velocity of gasoline can be considerably different from that of iso-octane, particularly at higher temperatures and pressures. Cruz et al. [14] and Farrell et al. [15] reported that aromatics have different flame speeds compared to alkanes. Therefore, the laminar burning velocities of PRF mixtures are different from gasoline laminar burning velocities and may induce errors during flame propagation simulations.

Pitz et al. [2] came to a consensus that iso-octane, n-heptane and toluene should be included in any gasoline surrogate. N-heptane and iso-octane were chosen since they are the primary reference fuel components and toluene was chosen because it is the most abundant aromatic in gasoline.

The laminar burning velocity of toluene has not been investigated as extensively as iso-octane and n-heptane with only few measurements having been presented [15–20]. For gasoline, even fewer measurements have been reported [10,21,22]. Gasoline is a complex fuel mixture, with a wide variation in composition between commercial gasolines (for example the composition depends on the season to have a good startability) and as a result there is no fixed laminar burning velocity for gasoline. On the other hand, when investigating if a particular surrogate is good enough to predict the behavior of gasoline, comparison has to be made with a real gasoline.

Published data of the laminar burning velocity are not always consistent with one another and the spread of the measured values often exceeds the reported experimental uncertainty, even for fuels which are investigated thoroughly like iso-octane and n-heptane. Galmiche et al. [12] showed that there are significant discrepancies between all the correlations for the laminar burning velocity of iso-octane/air mixtures and that the differences are mainly due to the different experimental setup and methodologies for data postprocessing. Laminar burning velocity measurements must still be improved and the influence of temperature, pressure and diluents on the laminar burning velocity has to be investigated in further detail. Recent measurements of the laminar burning velocity of a commercial gasoline, iso-octane, n-heptane and toluene were performed by Dirrenberger et al. [23] using the heat flux method. Measurements of laminar burning velocities of iso-octane and n-heptane have previously been performed by van Lipzig et al. [4] using a similar heat flux setup as the present work. The results by Dirrenberger et al. are systematically lower than what was reported by van Lipzig et al. by a few cm/s, this discrepancy is larger than the stated experimental error. The goal of the present work was: first, to provide accurate experimental laminar burning velocity data for a (well characterized) gasoline and the gasoline surrogate components iso-octane, n-heptane and toluene and compare the experimental data with numerical simulations, previous data from the same setup [4] and data from the literature; second, to investigate the temperature dependence of the laminar burning velocities; and third, find a surrogate that can match the laminar burning velocity of the studied gasoline. Due to the differences between the results of Dirrenberger et al. [23] and van Lipzig et al. [4] laminar burning velocities of iso-octane and n-heptane were revisited in the present study, and in addition a wider temperature range was covered (298–358 K). The experimental setup has been subject to some improvements since the measurements of van Lipzig et al. [4] and the new results are therefore considered more reliable as discussed in the following.

2. Experimental setup

The measurements were performed using the heat flux method on a perforated plate burner. The heat flux method for the stabilization of adiabatic premixed laminar flames on a flat flame burner has been proposed by de Goey et al. [24] and further developed by van Maaren and de Goey [25]. This method was extensively used for measuring laminar burning velocities of gaseous fuels [25,26]. A detailed description of the method and associated experimental uncertainties for gaseous [27,28] and liquid [4,29] fuels have been published previously. Important features of the method are, therefore, only shortly outlined in the following. The present experimental rig is similar to that used by van Lipzig et al. [4] and Vancoillie et al. [30]. The experimental setup for the adiabatic flame stabilization using the heat flux method is shown in Fig. 1. A 2 mm thick burner plate perforated with small holes (0.5 mm in diameter) is attached to the burner outlet. The burner head has a heating jacket supplied with thermostatic water to keep the temperature of the burner plate constant. During the experiments, this temperature was fixed at 368 K. The plenum chamber has a separate temperature control system supplied with water at a temperature, which enables a temperature range of the fresh gas mixture from 298 to 358 K. The heating jacket keeps the burner plate edges at a certain temperature higher than the initial gas temperature, thus warming the (unburned) flow of gases. Conductive heat transfer of the flame to the burner plate cools the gas flow on its turn. When the flow rate of the gas mixture is changed, an appropriate value of the gas velocity can be found to nullify the net heat flux. In this case, the radial temperature distribution in the burner plate is uniform and equal to the temperature of the heating jacket. A theoretical analysis of the heat flux method has been given by de Goey et al. [24,25] where it was shown that the temperature profile of the burner plate can be approximated by a parabolic function

$$T_p(r) = T_c + Cr^2 \tag{1}$$

where $T_p(r)$ is the mean temperature of the perforated plate (averaged over the burner thickness) at radial position r. T_c is the thickness-averaged temperature of the perforated plate at the center of the plate ($r = 0$). A series of thermocouples attached to the burner plate allow for measuring the temperature distribution at different radial positions. A polynomial fit is performed to find the heat flux constant C in Eq. (1). Close to $C = 0$, the heat flux constant C can be well-approximated by a linear fit. This was the case for all flames considered in this study. The interpolated flow velocity at which the net heat flux was zero is shown to be the adiabatic flame burning velocity of the unburned gas mixture [24,25]. A mixing panel shown in Fig. 1 was used to provide a controlled flow of the vaporized fuel and air, at the required equivalence ratio. The key part of this mixing panel is the CORI-FLOW liquid mass-flow controller (MFC) connected to the controlled evaporator mixer (CEM), both from Bronkhorst B.V. The liquid fuel flow from the fuel reservoir, pressurized by nitrogen, is metered by the CORI-FLOW MFC and fed to the CEM. Part of the air flow controlled by the gas MFC-1 is used as a carrier gas to facilitate vaporization at temperatures up to 473 K. Another part of the air flow controlled by the gas MFC-2 and mixed downstream is varied to provide the required mixture composition. For the measurements reported in this study, the tube connecting the controlled evaporator mixer to the burner was a heated tube to avoid condensation of the fuel in the way to the plenum chamber.

3. Error assessment

Two major sources of experimental uncertainties for gaseous fuels pertinent to the heat flux method were identified as (1)
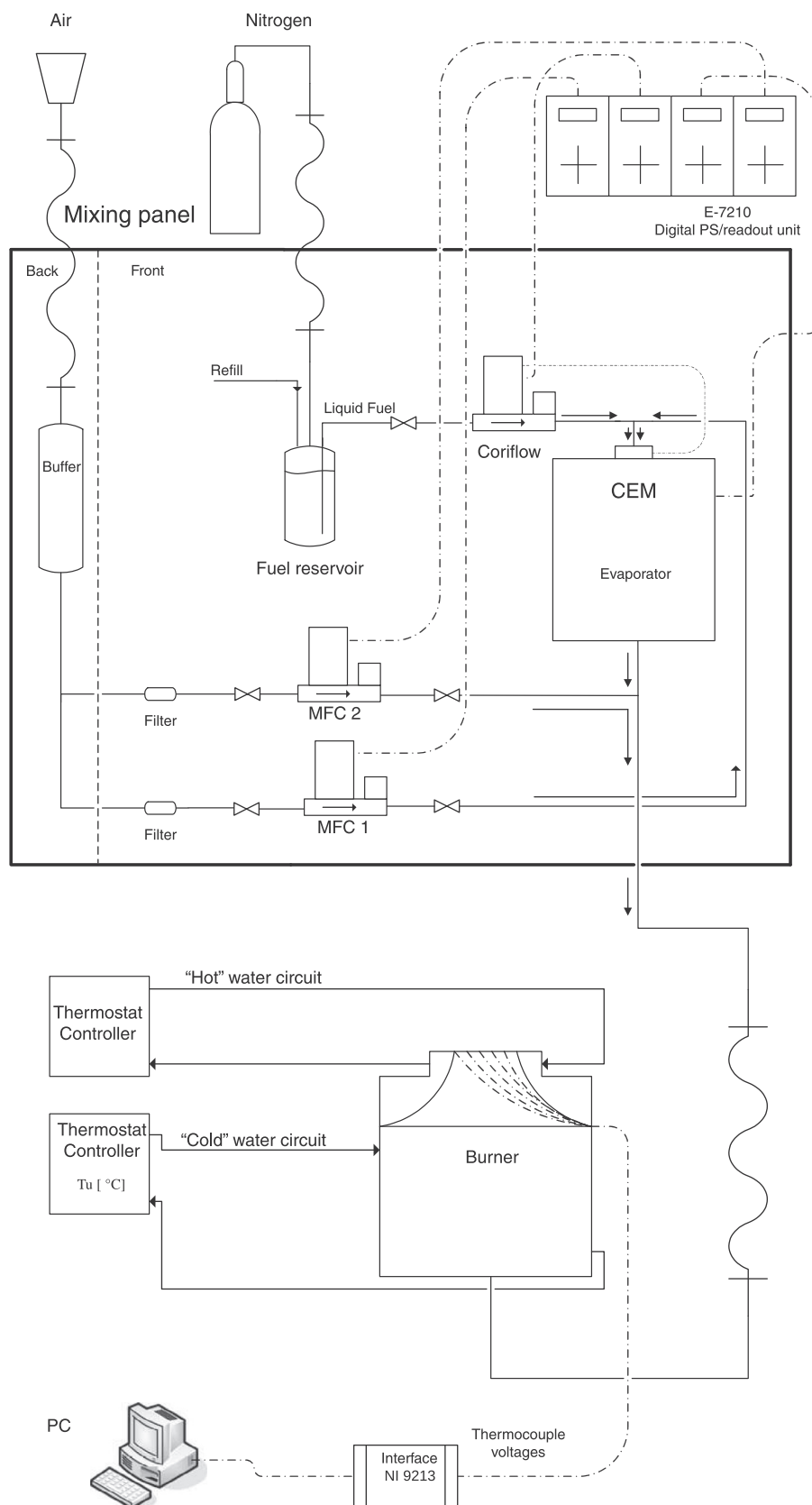
Fig. 1. Experimental heat flux setup for liquid fuels.

irregular thermocouple placement in the burner plate and (2) inaccuracy in the mass-flow control. Detailed analysis of these uncertainties was performed earlier [27,28] and showed that the overall accuracy of the burning velocity measurements in mixtures near stoichiometry could be better than ±0.8 cm/s and the relative accuracy of the equivalence ratio was found to be typically below

1.5% [29]. Additional possible sources of experimental uncertainties associated with liquid fuels are the following: (1) variable flow ratio of the air between MFC-1 and MFC-2, (2) influence of the CEM operating temperature, (3) dissolution of nitrogen in the liquid fuel, (4) fuel purity, (5) influence of the temperature of the heated tube between the evaporator and the burner and (6) stability of the CORI-FLOW operation. The first four additional sources were assessed experimentally as described in Ref. [29], and relevant procedures were repeated for the present installation [4]. It was shown that the ratio of the flows via MFC-1 (carrier gas for the CEM) and MFC-2 does not affect the measured burning velocity within the expected accuracy of the measurements. No influence of the CEM operating temperature was observed when it was set well above boiling temperatures of the fuels. The purity of the fuels, delivered in sealed bottles, was better than 99.5% for iso-octane, 99% for n-heptane and 99.9% for toluene and the refilling time was very short to avoid impurities in the fuel.

In the present work the gas mixture was transported from evaporator to burner through a heated tube, in contrast to the work of van Lipzig et al. where an insulated but not heated tube was used. Although no droplets were observed during the measurements without the heated tube, a comparison of results obtained with and without heated tube strongly suggested that some condensation (probably of trace components) did occur without it, especially for toluene and gasoline. For instance in the measurements on toluene without the heated tube, the burning velocities for rich mixtures were too high indicating that the fuel–air mixture was probably leaner than set because of condensation. From this experience we conclude that one of the reasons of the higher results for iso-octane and n-heptane obtained by van Lipzig et al., compared to Dirrenberger et al. and the present study, can possibly be a result of condensation and thus leaner gas mixtures than expected.

For the stability of the CORI-FLOW operation, it was found that vibrations of the water heaters to control the temperature of the fuel/air mixture had an influence resulting in unstable laminar burning velocity measurements, especially at lower flows. After eliminating the vibrations of the water heaters, stable operation was observed for all equivalence ratios and temperatures.

Both of the described changes, installation of heated tube and elimination of vibrations, are expected to decrease the uncertainty in mixture composition and thus give a more reliable result for the laminar burning velocities. Condensation of the fuel in the tube between the evaporator and the burner is more likely to happen for rich equivalence ratios resulting in an overestimation of the laminar burning velocity. If because of vibrations, the actual fuel rate is different than set, the laminar burning velocity is influenced and can lead to over- or underestimation of the true laminar burning velocity.

Another experimental difficulty associated with the heat flux method is related to the important assumption of the symmetry of the temperature distribution in the burner plate described by Eq. (1). In fact all previous studies employing this method rely on point-wise temperature measurements using thermocouples or thermographic phosphor technique [31]. Some scatter in the thermocouple readings were attributed to the different depth of their placement in the burner plate holes [28]. Bosschaart and de Goey proposed linear correction to compensate for this effect that reduced residual deviation of the thermocouple reading from the expected parabolic profile less than 0.5 K [28]. However, if for some reasons the thermal conductivity on the edges of the burner plate is not uniform there could be systematic deviations from the symmetry that may lead to systematic errors in the burning velocity measurements. Then switching off one of the most affected thermocouples may lead to significant deviation in the approximated temperature profile as observed by van Lipzig et al. [4]. This deviation, though not significant, was actually observed by Bosschaart

and de Goey [28]: even after correction the residuals are not zero for zero value of the parabolic coefficient C (see Eq. (1)). Moreover, lack of expected symmetry was recently found employing thermographic technique [32] when complete burner plate surface was covered by a phosphor. One may conclude that the measurements of van Lipzig et al. [4] were probably affected by the non-symmetry effect that was manifested in significant over-evaluation of the burning velocities obtained in that study.

Previous work on liquid fuels estimates the overall accuracy of the heat flux method due to these uncertainties to be better than ±1 cm/s [4,30]. While the same type of error estimation is used for the uncertainty in the mass-flow control, a different method has been used to estimate the error due to the thermocouples. The new method calculates the error due to the polynomial fit of the temperature distribution as a function of the radial placement of the thermocouples. To calculate this error, the standard deviation of the polynomial fit on the thermocouples readings is divided by the slope of the linear fit to find the flow velocity at which the net heat flux was zero. In Fig. 2, the black vertical error bars are the standard deviations of the polynomial fits on the thermocouples readings. These errorbars are taken into account in the polynomial fit to the data, giving an error on the laminar burning velocity, in Fig. 2 this error is represented by the red horizontal error bar. With this method, the overall accuracy of the measurements presented in this work is commonly better than ±1 cm/s. Only for mixtures with an equivalence ratio of 1.3, the error was larger (maximum ± 1.4 cm/s) as a result of the slope of the linear fit to find C = 0 being smaller. Because for these rich mixtures, the flame structure is too unstable near the velocity of the laminar burning velocity, extrapolation from lower burning velocities is used. As a result, the standard deviation of the polynomial fit on the thermocouples readings is larger.

4. Kinetic modelling

The measurements of the pure fuels are compared to simulations using two chemical oxidation mechanisms: the model of Andrae [33] and the model of Mehl et al. [34]. These models are commonly used in CFD and engine simulations to calculate the
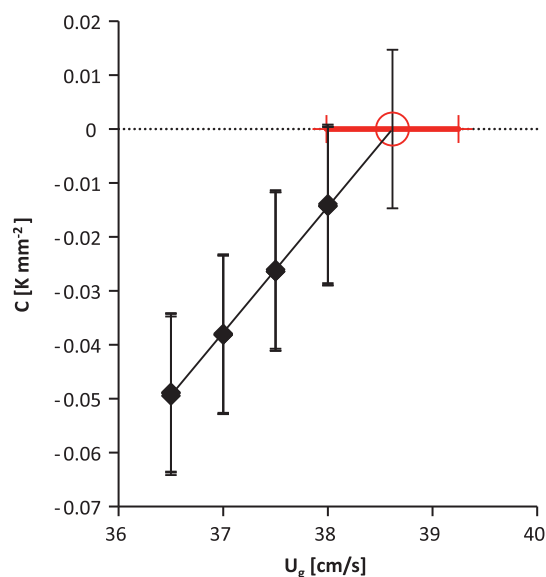

Fig. 2. Heat flux constant C as a function of the unburned gas velocity U_g (T_0 = 318 K, and p = 1 atm). The horizontal red line is the error on the laminar burning velocity resulting from the error of the polynomial fit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

laminar burning velocity. The model of Andrae [33] is a semi-detailed mechanism containing 150 species and 759 reactions. It consists of a detailed description of toluene oxidation and skeletal mechanisms of iso-octane and n-heptane. The model of Mehl et al. [34] is a reduced version of a detailed chemical kinetic mechanism for the simulation of gasoline surrogate mixtures. This reduced version was made for engine numerical applications and considers 312 species. The original detailed model has been assembled from existing LLNL mechanisms for n-heptane, iso-octane [35], toluene and C5-C6 olefins [36].

For the modeling of adiabatic premixed flames, the one-dimensional chemical kinetics code CHEM1D was used [37]. This code was developed at Eindhoven University of Technology and employs the EGLIB complex transport model, including multi-component transport and thermal diffusion. In each case, the solution was calculated using the exponential differencing technique in a grid consisting of 200 points, with most of the detail centered at the inner flame layer. Radiation was neglected, and solver convergence was confirmed by ensuring that all residuals were below 10^{-10} and the laminar burning velocity had reached a stable value.

5. Results and discussion

5.1. Gasoline

Laminar burning velocities have been measured for a gasoline (Exxon 708629-60) without oxygenates at 298, 318, 328, 338, 348 and 358 K. The gasoline has been analyzed and was found to be composed of 10.37% v/v n-alkanes, 40.2% v/v iso-alkanes, 34.39% v/v aromatics, 9.39% naphtenes and 5.65% v/v olefins. Detailed composition of the gasoline could be found in Electronic Supplementary Material.

Fig. 3 compares the measurements at 358 K with the data found in literature for commercial gasolines. There is a good agreement both with the data of Dirrenberger et al. [23], who used the same method to measure the laminar burning velocity, and with the data of Zhao et al. [21] (at 353 K) who used the stagnation jet-wall flame configuration and Particle Image Velocimetry. It is expected that the differences are influenced by the composition of the gasoline. The gasoline used by Dirrenberger et al. [23] was provided by TOTAL (Ref. IFPEN: TAE 7000) and contained oxygenated compounds which could explain the higher burning velocities around equivalence ratio 1.0–1.1 if the oxygenated compounds were alcohols.

The most widely used correlation describing the effect of initial temperature on the burning velocity:

$$u_l = u_{l0}\left(\frac{T_u}{T_{u0}}\right)^{\alpha} \tag{2}$$

where u_l is the laminar burning velocity and T_u is the unburned mixture temperature, was used in this or equivalent form since 1950s, e.g. [38]. The subscript 0 refers to the values at reference conditions (usually 298 K and 1 bar). α represents the power exponent of the temperature dependence. The temperature dependence can be expressed by plotting the laminar burning velocities as a function of the temperature using log–log scales. The slope of the measurements represents the power exponent of the temperature dependence and can be compared to the power exponents used in correlations for laminar burning velocity.

Measured laminar burning velocities of gasoline–air flames at atmospheric pressure and different initial temperatures are shown in Fig. 4 using log–log scales. Apart from the experimental data represented by symbols, lines are included to show the best fits to Eq. (2). In Fig. 5, the derived power exponents α are compared to the power exponent of other correlations used for the laminar burning velocity of gasoline in simulation programs.
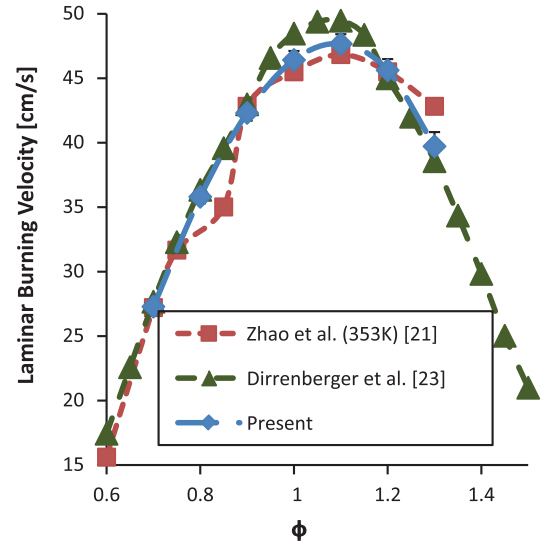

Fig. 3. Laminar burning velocities of gasoline at 358 K.

In comparison to the present measurements, the correlation by Metghalchi and Keck [7] and the correlation used in GT-power, the industry standard for engine simulations, use higher α values. The correlation used in GT-power is based on the publication of Kimitoshi et al. [39]. The correlation by Gülder [40] is based on laminar burning velocity measurements of iso-octane and is used in simulation programs to calculate the burning velocities of gasoline. This correlation has α values that are lower than the results of the present study imply and does not include the effect of the equivalence ratio on the power exponent. Metghalchi and Keck and Gülder both used closed vessels and spherical flames to measure the laminar burning velocity but did not take flame stretch and instabilities into consideration. Failing to perform stretch corrections for the spherical flames inside these closed vessels can lead to over- or underestimation of the true laminar burning velocity depending upon the sign of the Markstein number resulting in different α
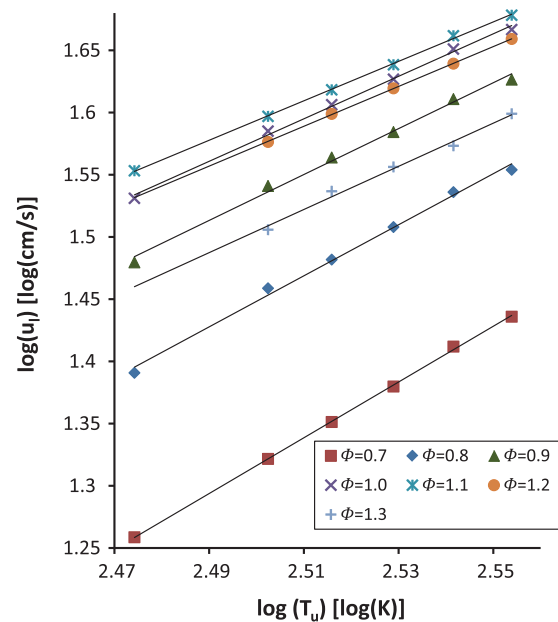

Fig. 4. Log–log plot of laminar burning velocities of gasoline–air flames at atmospheric pressure and different initial temperatures. Symbols, experiments; lines, linear fits.
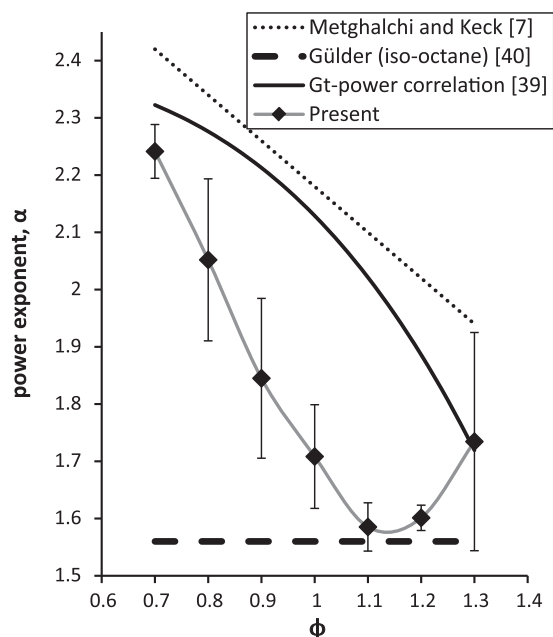
Fig. 5. Comparison between the power exponent α from measurements and the power exponent α used in correlations of the burning velocity of gasoline.

exponents [3]. We can conclude that none of the correlations is able to reproduce the temperature dependence measured for this gasoline, with a minimum around the equivalence ratio of peak burning velocity. A second order polynomial as function of the equivalence ratio can be used to represent the power exponent α: $\alpha = 5.93 - 7.52\Phi + 3.28\Phi^2$ in the range $0.7 < \phi < 1.3$.

5.2. Gasoline surrogate components

Laminar burning velocities have been measured for the gasoline surrogate components iso-octane, n-heptane and toluene at 298, 318, 328, 338 and 358 K. In Figs. 6–8, there is a comparison between the present measurements and data from literature at respectively 298 K and 358 K. For the clarity of the figures, only selected data from the literature is included. For iso-octane at 298 K, there is again a good agreement with the measurements of Dirrenberger et al. [23] who used the same method. The measurement are a few cm/s lower than the previous measurements on the same setup performed by van Lipzig et al. [4]. At 358 K, there is a very good agreement with the measurements of Dirrenberger et al. [23]. The measurements of Bradley et al. [3] who used spherically expanding flames to measure flame speeds compare well for rich mixtures but are higher for lean mixtures.

For n-heptane and toluene, the same trend as for iso-octane is seen. There is a good agreement with the measurements of Dirrenberger et al. [23] and there are some differences when comparing to other data. For n-heptane at 298 K, the measurements of Dirrenberger et al. are almost the same and there is also a good agreement with the measurements of Huang et al. [8] and Davis et al. [11]. Only for toluene at 298 K, the difference between the measurements of Dirrenberger et al. and the present measurements is more marked. Dirrenberger et al. did measurements at 298, 358 and 398 K and as a result, it is possible to compare the temperature dependence of the present measurements and the measurements performed by Dirrenberger et al. On Fig. 9, the laminar burning velocities are shown as a function of the temperature on log–log scales, only for a few equivalence ratios for the clarity of the figure. It is clear from Fig. 9, that the measurements of Dirrenberger et al. follow more or less the same trend as the present measurements for 358 K and 398 K but deviate for 298 K. Based on this
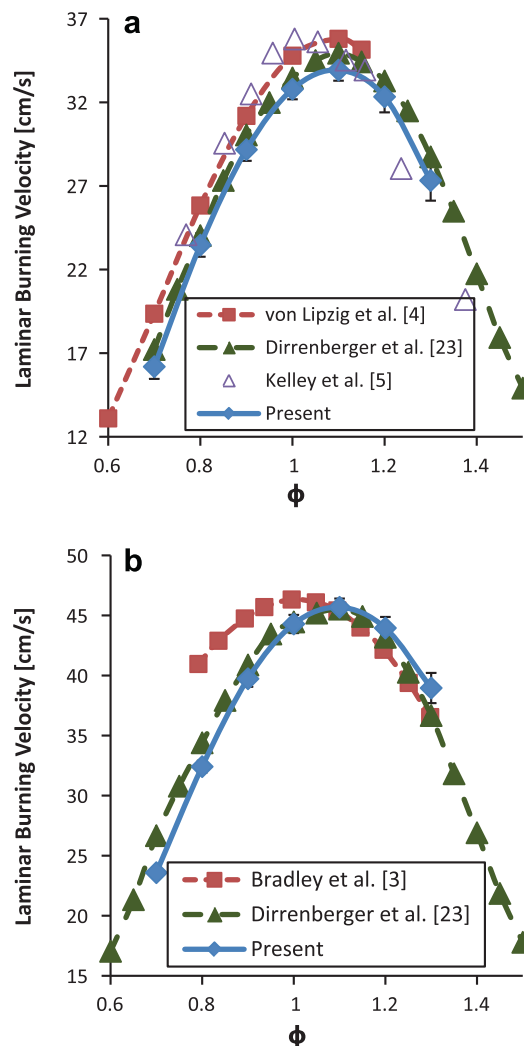

Fig. 6. Laminar burning velocities of iso-octane at 298 K (a) and 358 K (b).

it seem likely that the laminar burning velocities of toluene at 298 K measured by Dirrenberger et al. are too high compared to the other measurements.

In Figs. 10–12, a comparison is made between two chemical oxidation mechanisms and the present measurements of iso-octane, n-heptane and toluene at 298 K and 358 K. For toluene and iso-octane, the model of Mehl et al. [34] predicts the laminar burning velocities better, especially for lean mixtures. For iso-octane, the model overpredicts the measurements but the qualitative dependence of the equivalence ratio is covered better than the model of Andrae [33] which underpredicts the laminar burning velocities for lean mixtures and overpredicts the laminar burning velocity for equivalence ratios in the region of 1.1–1.2.

For n-heptane, both models cover the dependence of the equivalence ratio in a good way but both models overpredict the laminar burning velocity. Here, the better agreement is for the model of Andrae.

In Fig. 13, the derived power exponents α of iso-octane are shown and compared to the power exponents of correlations of the laminar burning velocity of iso-octane/air mixture and to the power exponents derived from the simulations with the model of Mehl et al. There is again a minimum around the equivalence ratio of peak burning velocity which is covered by none of the correlations. The correlation of Metghalchi and Keck [7] and the correlation of Galmiche et al. [12] predict a linear decrease of α as function of the equivalence ratio whereas the correlation of Gülder
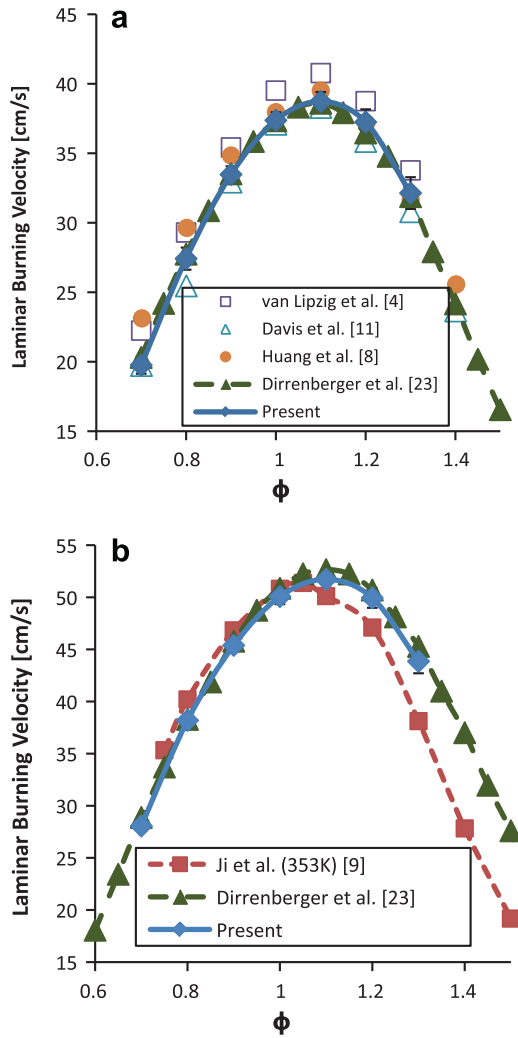
Fig. 7. Laminar burning velocities of n-heptane at 298 K (a) and 358 K (b).
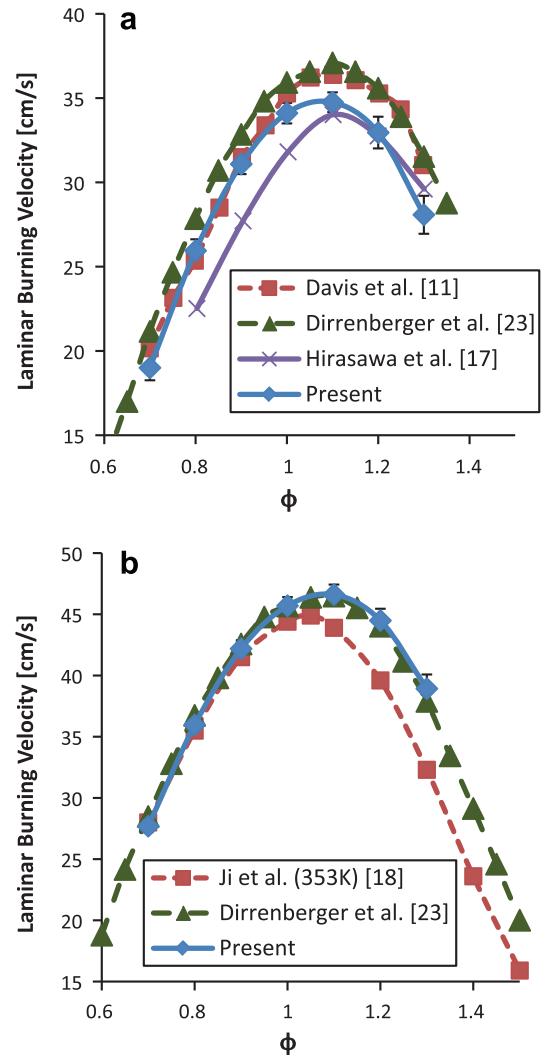

Fig. 8. Laminar burning velocities of toluene at 298 K (a) and 358 K (b).

[40] does not include the effect of the equivalence ratio on the power exponent. The minimum around the equivalence ratio of peak burning velocity is well covered by to model of Mehl et al. and there is a good agreement for equivalence ratios from 0.8 to 1.2. In Fig. 14, the derived power exponents α of iso-octane, n-heptane and toluene are shown together. All three fuels have a minimum around the equivalence ratio of peak burning velocity.

5.3. Gasoline vs. TRF

Measurements of a toluene reference fuel (iso-octane, n-heptane and toluene) have been performed to see if a toluene reference fuel can be used to match the laminar burning velocity of a commercial gasoline. Therefore, a correct mixing ratio of the mixture of iso-octane, n-heptane and toluene has to be found. Depended on the specific property that the surrogate should be able to predict, the method to find the correct mixing ratio of the different fuels will be different. For some applications the toluene reference mixture is formulated to match the commercial gasoline regarding C/H ratio, molecular mass, lower heating value, boiling point, density or auto-ignition properties such as the research octane number or the motor octane number [41]. In the present study the composition of the toluene reference fuel was based on the laminar burning velocities of the pure fuels iso-octane, n-heptane and toluene (as reported above) and the laminar burning
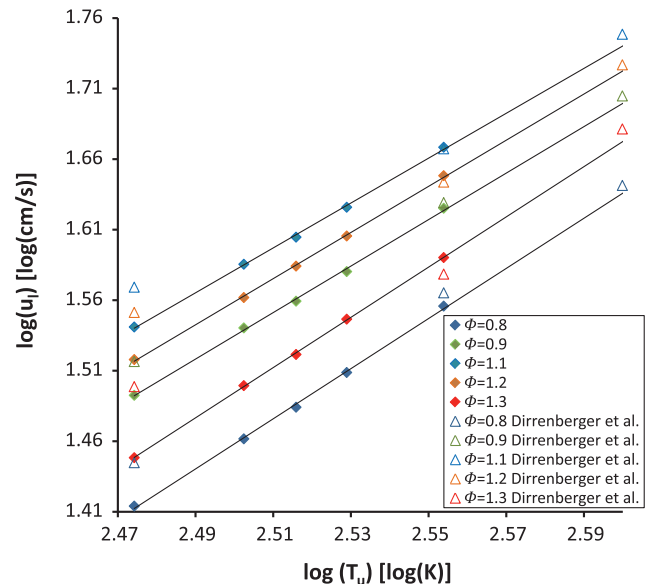

Fig. 9. Log–log plot of laminar burning velocities of toluene–air flames at atmospheric pressure and different initial temperatures. Diamonds, present experiments; Circles, measurements [23]; lines, linear fits of present measurements.
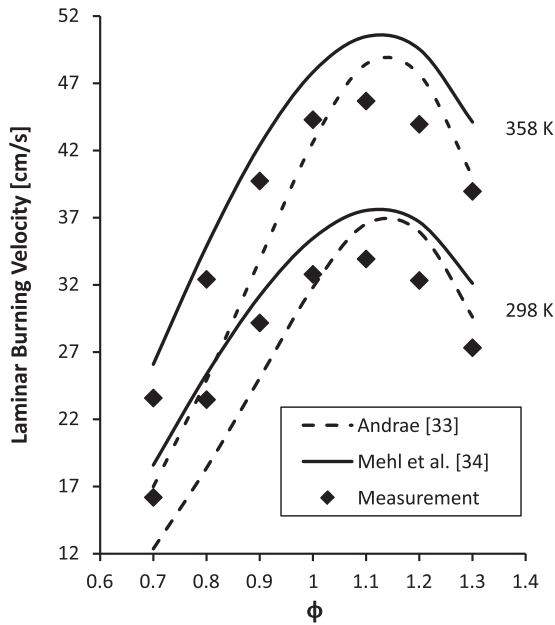
Fig. 10. Comparison of the present measurements and predictions of kinetic models for the laminar burning velocity of iso-octane at 298 K and 358 K.

Fig. 12. Comparison of the present measurements and predictions of kinetic models for the laminar burning velocity of toluene at 298 K and 358 K.

velocities of the gasoline at different temperatures. A simple mixing rule for the laminar burning velocity was applied to predict which mixture of iso-octane, n-heptane and toluene could have a similar laminar burning velocity of gasoline for the whole temperature range. Simple mixing rules were investigated for ethanol–hydrocarbon fuels by Sileghem et al. [42] to have fast calculation times in simulation programs and predicted the laminar burning velocity of the fuel blends accurately. Burning velocities are mostly governed by flame temperature, activation energy, and, to a certain extent, the transport properties [17]. There is thus a kinetic, a thermal and a transport effect. It was found that the flame temperature is the dominant factor for laminar burning velocity of the ethanol–hydrocarbon blends and three mixing rules gave very good results: a mixing rule based on the energy fraction of the components, a
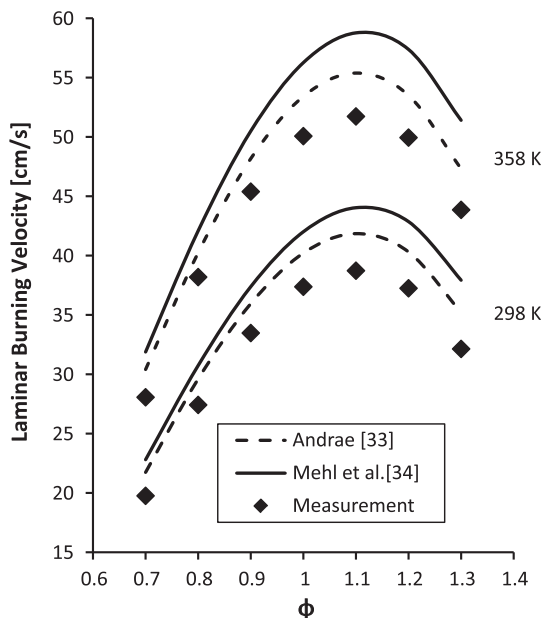
mixing rule proposed by Hirasawa et al. [17] and a mixing rule using the principle of Le Chatelier's flame theory. One of these mixing rules can be used to calculate the mixture of iso-octane, n-heptane and toluene that could match the laminar burning velocity of gasoline. For the fuels used in this study, the differences between the results of the different mixing rules are small and here, the energy fraction mixing rule was used:

$$u_{l,\text{blend}}(\Phi) = \sum_{i=1}^{n} \gamma_i \cdot u_{l,i}(\Phi) \tag{3}$$

where γ_i is energy fraction of the fuel and u_l represents the laminar burning velocity.

Fig. 11. Comparison of the present measurements and predictions of kinetic models for the laminar burning velocity of n-heptane at 298 K and 358 K.
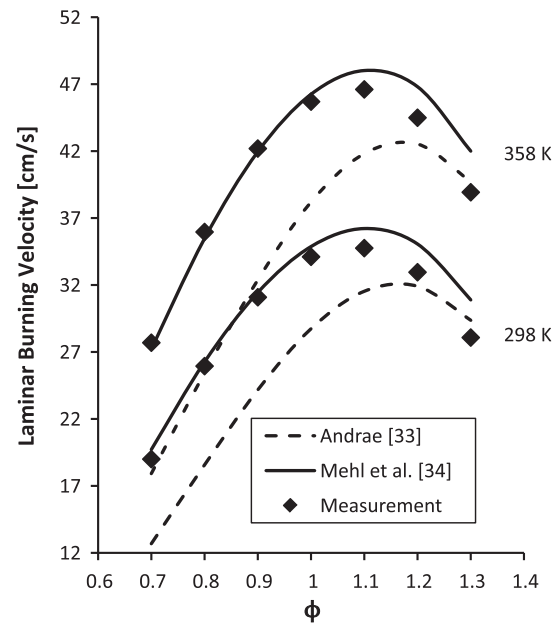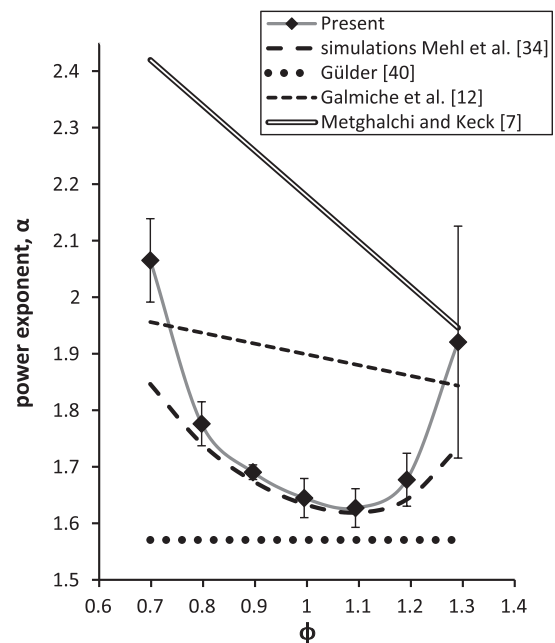

Fig. 13. Comparison between the power exponent α of iso-octane from the present measurements and the power exponent α derived from the model of Mehl et al. and used in correlations of the burning velocity of iso-octane.
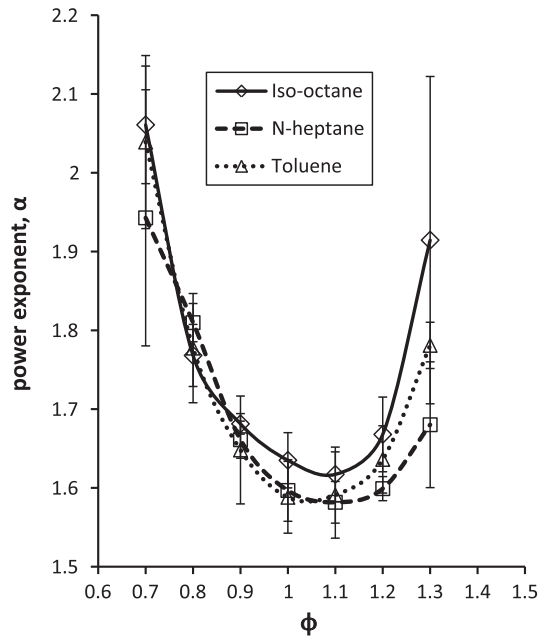
Fig. 14. Power exponent α of iso-octane, n-heptane and toluene from measurements.

Fig. 15. Comparison between the laminar burning velocity of iso-octane, n-heptane, toluene, gasoline and the toluene reference fuel at 338 K together with the prediction of the energy fraction mixing rule.

The energy fraction can be calculated as follows:

$$\gamma_i = \frac{\Delta_c H_i^\circ \cdot x_i}{\sum_{i=1}^n \Delta c H_i^\circ \cdot x_i} \tag{4}$$

where $c H_i^\circ$ is the heat of combustion of the mixture components. x_i is the mole fraction of the fuel components. By changing the fraction of the components in the mixing rule, it was found that a mixture of 1/3 iso-octane, 1/3 n-heptane and 1/3 toluene on volume basis could have a similar laminar burning velocity and this mixture had the advantage that it was easy to blend on volume basis decreasing the chances of errors.

In Fig. 15, a comparison between the laminar burning velocities of gasoline, iso-octane, n-heptane, toluene and the toluene reference fuel is shown. It is clear that for lean mixtures, a combination of iso-octane and n-heptane could be sufficient to reproduce the laminar burning velocity of gasoline but that the same fuel blend will not be able to reproduce the laminar burning velocities for rich mixtures because of the aromatics in gasoline. This was also found by Jerzembeck et al. [10]. They found that the laminar burning velocity for lean mixtures of a commercial gasoline can be matched by a PRF mixture with a research octane number of 87 but deviations were observed for stoichiometric and rich mixtures. To cover a bigger equivalence ratio range, a TRF is needed. From Fig. 15, one can conclude that the mixture of 1/3 iso-octane, 1/3 n-heptane and 1/3 toluene on volume basis is capable of matching the laminar burning velocity of gasoline and that the energy fraction mixing rule is accurate enough to predict the laminar burning velocity of toluene reference fuels although the differences between all the fuels are relatively small.

In Fig. 16, the laminar burning velocity of gasoline is shown for different temperatures together with the laminar burning velocity of the TRF and the predictions made by the energy fraction mixing rule based on the burning velocities of iso-octane, n-heptane and toluene. From this figure we can conclude that for these laminar burning velocities at atmospheric pressure, this mixture of iso-octane, n-heptane and toluene is able to reproduce the laminar burning velocity and the temperature dependence of the commercial gasoline. The power exponents of the toluene reference fuel and
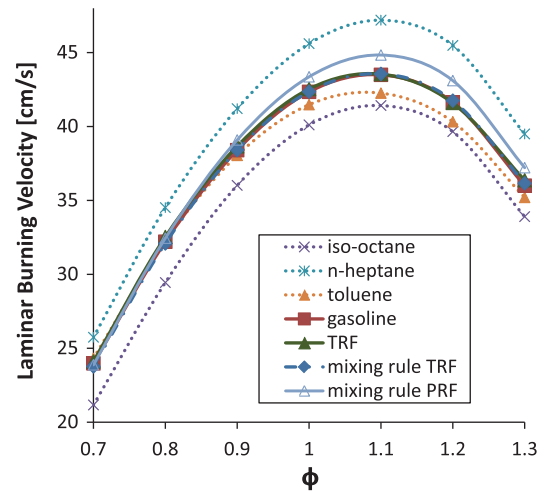
the gasoline are compared in Fig. 17. For most of the equivalence ratios, both fuels have similar temperature dependence. Although the laminar burning velocities of this toluene reference fuel are in correspondence with the laminar burning velocities of the studied gasoline, this mixture of iso-octane, n-heptane and toluene will not be able to predict all fuel properties, engine characteristics or laboratory data of this gasoline such as ignition delay, evaporation characteristics and emissions. Therefore, specific surrogates should be used to emulate specific properties.

Laminar burning velocities of all the measurements at different initial temperatures are summarized in Electronic Supplemental Material.

6. Conclusion

Measurements of the laminar burning velocity have been done for gasoline, iso-octane, n-heptane, toluene and a toluene reference fuel for a wide range of temperatures at atmospheric pressure using the heat flux method on a perforated plate burner. The temperature dependence of the laminar burning velocity as a function of the equivalence ratio has been shown for gasoline, iso-octane,
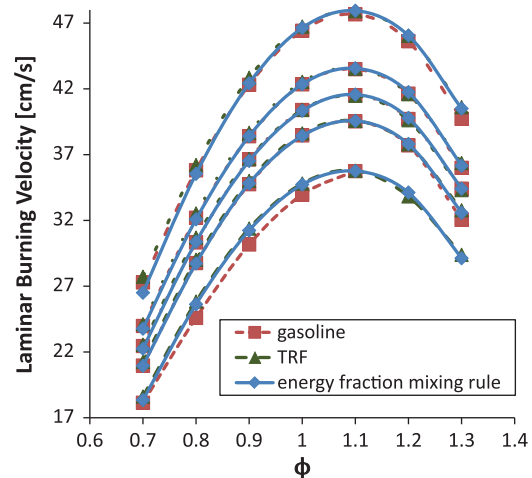

Fig. 16. The laminar burning velocity of gasoline and the toluene reference fuel at 298, 318, 328, 338 and 358 K together with the predictions of the energy fraction mixing rule.
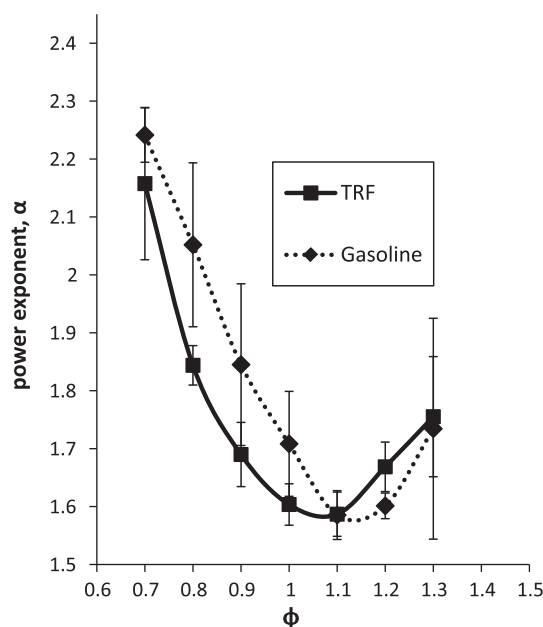
Fig. 17. Comparison between the power exponent α of gasoline and the power exponent α of the toluene reference fuel.

n-heptane and toluene. All fuels have the temperature dependence with a minimum around the equivalence ratio of peak burning velocity. The temperature dependence of gasoline has been compared to current correlations for gasoline but none of the correlations captured the temperature dependence of gasoline with a minimum around the equivalence ratio of peak burning velocity.

A mixing rule based on the energy fraction has been used to calculate the composition of a mixture of iso-octane, n-heptane and toluene that could represent the laminar burning velocity of the gasoline studied. Based on the mixing rule, it was found that a mixture of 1/3 iso-octane, 1/3 n-heptane and 1/3 toluene should be close to the laminar burning velocity of the gasoline. Measurements of this toluene reference fuel reproduced the laminar burning velocity of the gasoline very well. The measurements of iso-octane, n-heptane and toluene have been compared to data from the literature and to simulations of two kinetic models. The agreement with the measurements of Dirrenberger et al. (who used the same method to measure the laminar burning velocity) was very good. For the kinetic mechanisms, none of the models could reproduce the laminar burning velocity of all the fuels and improvements are thus still needed.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2013.05.049.

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