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NUMERICAL MODELING THE LAMINAR BURNING VELOCITY OF GASOLINE SURROGATES

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Abstract. *This work aims to the numerical study of the laminar burning velocity of gasoline/air combustion by three different kinetic models from literature, and to observe the effect of adding methanol in these analyses. Numerical simulations were carried out over a wide range of conditions to compare the capacity of all three mechanisms in modeling the laminar burning velocity of a gasoline surrogate. All mechanisms showed a good approach to the experimental data from literature, although one of them had a substantial divergence of laminar velocity when the results were plotted in function of pressure. A ternary and five-components gasoline surrogates were compared and both produced very similar results. Also, the effect of increasing the concentration of oxygen in the oxidizer was investigated, and addition of 1% of oxygen resulted in substantially higher velocities. Finally, the methanol addition on gasoline only affects significantly the results in a rich mixture and high methanol concentrations, resulting in higher laminar burning velocities.*

Keywords: *gasoline surrogate, gasoline/methanol blend, laminar burning velocity, gasoline kinetic model*

1. INTRODUCTION

Nowadays, gasoline is still a very useful petroleum-based fuel. However, it has very complex chemistry and physics since it is composed of hundreds of hydrocarbons, which complicates experimental and numerical analysis (Mannaa *et al.*, 2016). So, some gasoline surrogates formed by a few components have been proposed such as the ternary surrogate n-heptane/iso-octane/toluene (Dirrenberger *et al.*, 2014) and the five-components surrogate hexane/2,3 dimethyl-2-butene/cyclohexane/isooctane/toluene (Wu *et al.*, 2017), which were studied to match the properties of the commercial gasoline TAE7000. These surrogates make possible to represent the gasoline fuel in a simple kinetic model and to numerically analyze the laminar burning velocity of this fuel over a wide range of conditions.

The physicochemical property laminar burning velocity characterizes a premixed flame and assumes a steady one-dimensional adiabatic free flame propagation in an infinite domain (Konnov *et al.*, 2018). It can be used to validate kinetic models, preview heat release of combustion, and to characterize the reactivity of the mixture fuel/oxidizer. Much experimental and numerical research about the laminar burning velocity of various fuel+air mixtures have been made. A detailed resume of the experimental and numerical laminar burning velocity of main single-component fuels, like hydrogen, methane, ethane, liquid alkanes, and alcohols-air mixtures, was presented by Konnov *et al.* (2018). The laminar burning velocities of gasoline and gasoline/oxygenate blends burning with air have been investigated by many authors such as Wu *et al.* (2017), Dirrenberger *et al.* (2014), Mannaa *et al.* (2016), Sileghem *et al.* (2014) and Elfasakhany (2015).

The current atmospheric issues induced the development of more efficient and 'green' fuels known as bio-fuels, such as ethanol and methanol. These alcohols can form a blend together with the gasoline to increase the octane rating of gasoline and, at the same time, to allow the fuel to burn more completely due to the oxygen present in the alcohol, resulting in more efficient combustion and less air-pollutant (Elfasakhany, 2015).

Therefore, the present work has as main objective to numerically analyze the capacity of three different kinetic mechanisms in correctly modeling the laminar burning velocity of a gasoline surrogate over a range of conditions, as also to analyze the effect in these velocities by adding methanol in the gasoline surrogate.

2. METHODOLOGY

Gasoline is composed of several hydrocarbons from C-4 to C-12, and some oxygenate whose small proportions can be neglected. These hydrocarbons consist basically of alkanes, olefins and aromatics compounds. Therefore, to model the kinetics of the commercial gasoline TAE7000, which is composed by 57% of alkanes, 8% of olefins and 35% of aromatics compounds as analyzed by Wu *et al.* (2017), two gasoline surrogates constituted only by hydrocarbons were used and their volumetric composition can be observed in Tab. 1. The gasoline surrogate 1 was proposed by Wu (2016) and consists of five pure compounds whose proportions were determined to better satisfy the distillation curve, octane rating, density, and other properties of the target commercial fuel. Already the ternary gasoline surrogate 2 showed in Tab. 1 was proposed by Dirrenberger *et al.* (2014) to match the autoignition properties, C/H ratio and normal boiling temperature of the TAE7000.

Table 1. Gasoline surrogates composition by liquid volume.

Gasoline Surrogate 1 (Wu, 2016)		Gasoline Surrogate 2 (Dirrenberger *et al.*, 2014)	
hexane	24.31%	n-heptane	13.7%
2,3 dimethyl-2-butene	8.15%	iso-octane	42.9%
cyclohexane	14.21%	toluene	43.4%
iso-octane	17.75%		
toluene	35.58%		

Three mechanisms were compared in modeling the kinetics of the gasoline surrogates/air combustion as presented in Tab. 2. Mechanism 1 is the JetSurF 2.0 (Wang *et al.*, 2010) that has been developed centered on n-dodecane and n-butyl-cyclohexane. Mechanisms 2 and 3 are reduced ones based on the detailed chemical kinetic mechanism presented by Mehl *et al.* (2011b), which was assembled from a n-heptane and iso-octane mechanism (Mehl *et al.*, 2009), and a toluene and C5-C6 olefins mechanism (Mehl *et al.*, 2011c).

Mechanism 2 was developed aiming to match the ignition delay time and laminar flame speed of an iso-octane, n-heptane, toluene and 1-hexene mixture, over a wide range of operating conditions, whereas mechanism 3 target the iso-octane, n-heptane, toluene, 2-pentene and ethanol as pure components and their mixtures. Moreover, mechanism 3 was validated for PSR extinction temperature and residence time, and auto-ignition delay of n-heptane-air mixtures, under various pressure and equivalence ratios.

Table 2. Mechanisms applied in modeling gasoline-surrogates/air combustion.

Mechanism	Number of Species	Number of Reaction	Reference
1	348	2163	Wang *et al.* (2010)
2	323	1488	Mehl *et al.* (2011a)
3	679	3479	Lu and Law (2009)

The *Chemkin Pro 19.0* software was run to model the laminar burning velocity for the gasoline/air and gasoline+methanol/air combustion, where a premixed laminar flame speed calculator operates to analyze the flame propagation.

3. RESULTS AND DISCUSSION

The modeled laminar burning velocities of gasoline surrogate 2 by all three mechanisms are presented in Fig. 1 where they can be compared to experimental results from Wu (2016); Wu *et al.* (2017), which used a specifically developed high-pressure combustion chamber, based on a preheated premixed Bunsen flame burner, to measure the laminar flame speed of multicomponent liquid fuels. These results are in function of the equivalence ratio and are presented for three preheating temperatures. The air was modeled with 20% oxygen to match the conditions of the experimental results. To compare the results from both gasoline surrogates, the laminar burning velocity varying with equivalence ratio were taken for both and it was observed that the differences in results are insignificant.

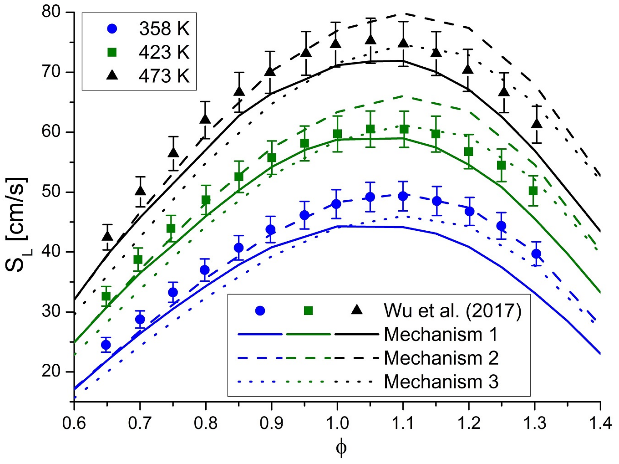

Figure 1. Laminar burning velocities in function of equivalence ratio for gasoline surrogate 2 burning with air ($O_2 = 20\%$), at P = 1 bar and three preheating temperatures.

In general, the mechanism that best follows the pattern of the experimental results is Mechanism 1, although it predicts lower values. Mechanism 2 is very close to Mechanism 1 for fuel-lean mixtures, but it predicts higher velocities for rich concentrations. Already mechanism 3 resulted in lower values for poor concentrations when compared to the other mechanisms, but it better approaches the experimental results for rich concentrations. As the temperature increases, these observations become more apparent. At $T = 358\ K$, mechanism 2 better matches the data. On the other hand, at higher temperatures, this mechanism is the farthest from the experimental results at high equivalence ratios, while mechanism 1 better follows the experimental curve.

In the interest to better observe the modeled laminar burning velocities by all three mechanisms, their variation with pressure was studied. The results are shown in Fig. 2 for three different equivalence ratios, where the modeled curves can be compared to the experimental data from Wu *et al.* (2017). Results from mechanisms 1 and 2 are very close to each other and the experimental data, although mechanism 2 better approaches the data at low pressures. Moreover, mechanism 3 is the most distant from the data and it becomes more clear at higher pressures.

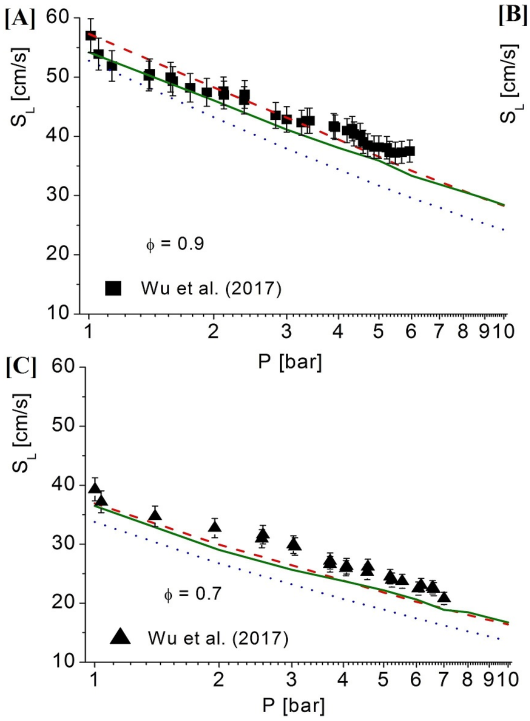

Figure 2. Laminar burning velocity in function of pressure for surrogate gasoline 2 burning with air ($O_2 = 20\%$), at T = 423 K and equivalence ratios [A] 0.9, [B] 0.8, and [C] 0.7.

The laminar burning velocity varying with equivalence ratio and pressure by using mechanism 1 was also modeled for an oxygen concentration of 21% in air. This analyzes had as objective to observe the sensibility of the results at oxygen concentration. The results for concentrations of 20% and 21% are shown in Fig. 3. The experimental data is found between the curves for 20% oxygen concentration (below data) and 21% oxygen concentration (above data).

In summary, a small increase in oxygen concentration results in significantly higher laminar burning velocities, independently of equivalence ratio or pressure. Moreover, the fact that the experimental data was obtained with a smaller concentration of oxygen in the air than usual must be considered to correctly observe the modeled combustion behavior.

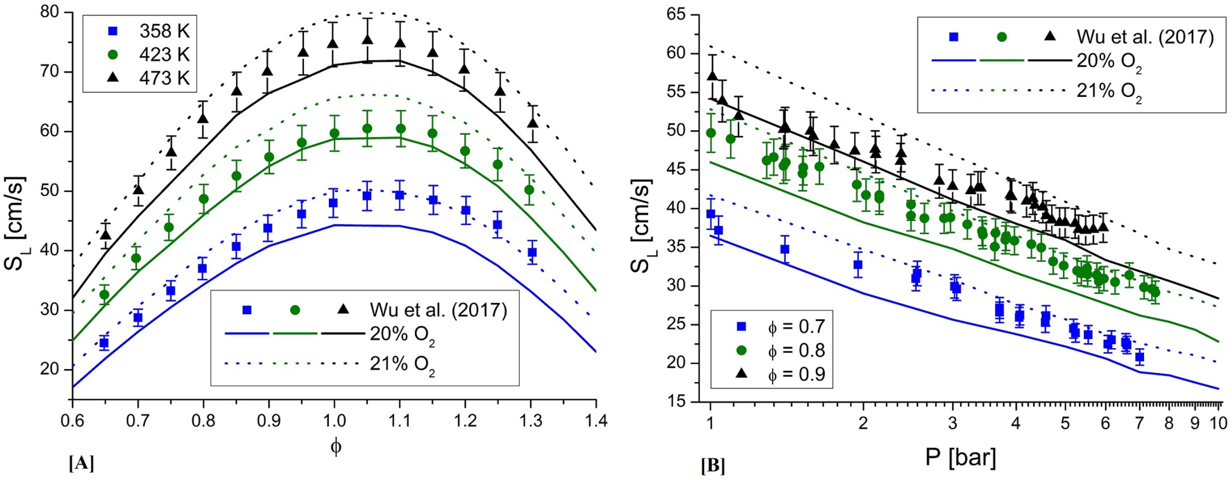

Figure 3. Modeled laminar burning velocity of surrogate gasoline 1 burning with air in function of [A] equivalence ratio at P = 1 bar and [B] function of pressure at T = 423 K, both compared to experimental results from Wu *et al.* (2017).

The numerical results presented so far were taken for surrogate gasoline 1 (Fig. 3), and for surrogate gasoline 2 (Fig. 1 and 2), without comparing them. To compare the results from both surrogates, the laminar burning velocity varying with equivalence ratio was taken for both as shown in Fig. 4. Observe that the differences in results are insignificant, although gasoline surrogate 2 presents smoothly lower velocities.

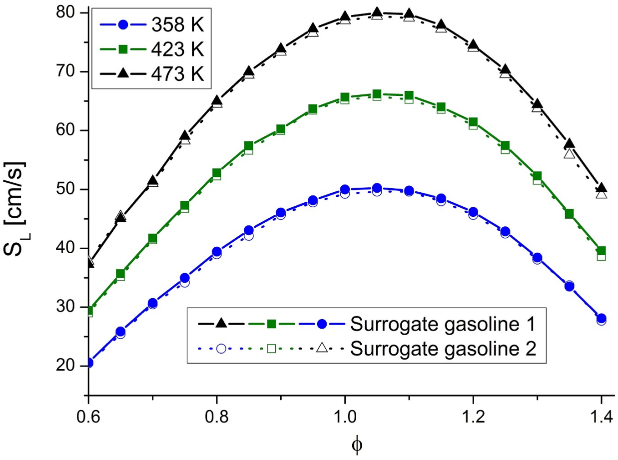

Figure 4. Comparison of modeled laminar burning velocity for surrogate gasoline 1 and 2 burning with air ($O_2 = 21\%$) at three preheating temperatures and P = 1 bar.

Gasoline/oxygenate blends have been studied by Wu *et al.* (2017), Dirrenberger *et al.* (2014), and many others.Wu *et al.* (2017) have analyzed the addition of anisole in a gasoline surrogate, concluding that the laminar flame velocity generally increases with the addition of oxygenates for a significant percentage added. However, when this percentage is less than 10%, the influence is negligible. Dirrenberger *et al.* (2014) have analyzed the addition of ethanol in commercial gasoline and a gasoline surrogate mixture, however, the small percentage added (15% of ethanol) resulted in a negligible change in laminar burning velocities.

The present work observed numerically the addition of methanol in gasoline surrogate 2. However, it was important to first observe the laminar burning velocity of pure methanol/air modeled by all three mechanisms analyzed in this work, as shown in Fig. 5 together with experimental data from Sileghem *et al.* (2014), Vancoillie *et al.* (2012), Saeed and Stone (2004), and Egolfopoulos *et al.* (1992).

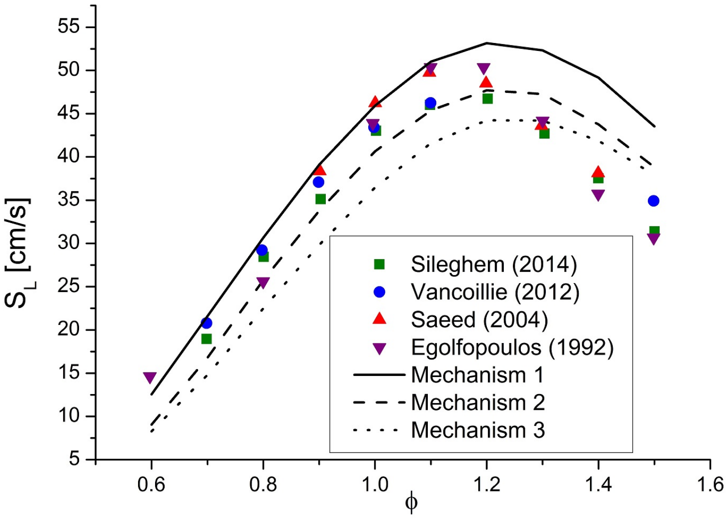

Figure 5. Laminar burning velocity for methanol burning with air ($O_2 = 21\%$) at standard conditions (P = 1 atm, T = 300 K).

Observe that mechanism 3 is the farthest from the experimental data for low equivalence ratios and does not correctly follow the behavior of the data curve. Mechanism 1 generally results in slightly higher velocities than experimental ones for small equivalence ratios (fuel-poor mixtures), but the differences increase significantly for higher equivalence ratios (fuel-rich mixtures). Mechanism 2 is the one which better matches the experimental results, presenting a slightly lower velocity for poor mixtures, and not much higher velocities for rich mixtures as mechanism 1.

Since mechanism 2 better approached the experimental data for the laminar burning velocity of pure methanol + air combustion, it was applied to the numerical simulation to observe the influence of methanol addition in surrogate gasoline 2 as shown in Fig. 6. Observe that for 25% of methanol addition in the fuel mixture, results in a small increase in the laminar burning velocities, and this increase grows as the methanol addition gets higher. However, these results are more significant as the mixtures become richer. For small equivalence ratios as 0.8 and lower, the changes are negligible.

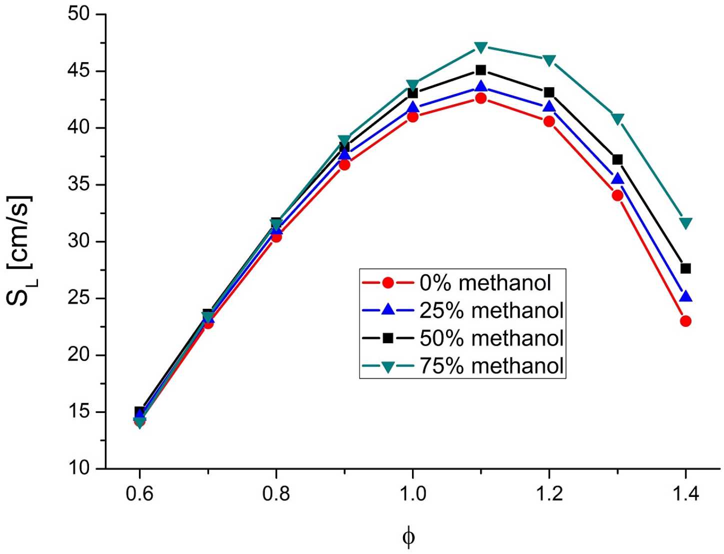

Figure 6. Laminar burning velocity of surrogate gasoline 2 + methanol burning with air ($O_2 = 21\%$) at standard conditions (P = 1 atm, T = 300 K).

4. CONCLUSIONS

The laminar burning velocities of a surrogate gasoline/air and pure methanol/air were modeled by three kinetic mechanisms in many operation conditions, varying pressure, equivalence ratio and preheating temperature. The results were compared to experimental data from literature, which showed that mechanism 3 is the less accurate when velocity is plotted against pressure, while mechanisms 1 and 2 are very close to each other and the experimental data. At low temperatures like 358 K, mechanism 2 better fits the experimental results, but it becomes less accurate at high temperatures and rich mixtures.

Moreover, the influence of oxygen concentration in air was analyzed, which showed that 1% more oxygen concentration increases significantly the laminar burning velocities. Also, the comparison of a ternary and a five-component gasoline surrogate resulted in very similar laminar velocities, the ternary surrogate just showed smoothly lower results.

Finally, the effect of adding methanol into a gasoline surrogate in the view of the laminar burning velocity was observed. As expected from literature, adding an oxygenate to a gasoline surrogate increases the laminar burning velocity mainly for rich mixtures. However, if the concentration of added oxygenates is very small such as lower than 20%, this change can be neglected.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

The list of references must be introduced as a new section, located at the end of the paper. The first line of each reference must be aligned at left. All the other lines must be indented by 0.5 cm from the left margin. All references included in the reference list must have been mentioned in the text.

References must be listed in alphabetical order, according to the last name of the first author. See the following examples:

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