Laminar Burning Velocities and Kinetic Modeling of a Renewable E-Fuel: Formic Acid and Its Mixtures with H₂ and CO₂

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ABSTRACT: Formic acid is a promising fuel candidate that can be generated by reacting renewable hydrogen with carbon dioxide. However, the burning characteristics of formic acid/air mixtures have not been extensively studied. Furthermore, due to its low reactivity, the addition of hydrogen to formic acid/air mixtures may help with improving burning characteristics. This paper presents the first extensive study of formic acid/air premixed laminar burning velocities, as well as mixtures with hydrogen and carbon dioxide. Unstretched laminar burning velocities and Markstein lengths of formic acid in air for two different unburnt gas temperatures and equivalence ratios are presented. Measurements of formic acid mixed with various proportions of hydrogen and carbon dioxide in air are also studied as a potential renewable fuel for the future. Experimental results demonstrate the low burning velocities of formic acid and the ability to significantly enhance flame speeds by hydrogen addition. A modified detailed kinetic model for combustion of formic acid and its mixtures with hydrogen is proposed by merging well-validated literature models. The proposed model reproduces the experimental observations and provides the basis for understanding the combustion kinetics of formic acid laminar premixed flames, as well as mixtures with hydrogen. It is shown that the HOCO radical is the principal intermediate in formic acid combustion, and hydrogen addition accelerates the decomposition of HOCO radical thereby accelerating burning velocities.

1. INTRODUCTION

Formic acid is widely associated with ants. The “sting” of ants is a sensation caused by formic acid injected into the skin. The injected chemical was first isolated by the distillation of ants. The resulting acidic liquid was called formic acid using the Latin word for “ant”, formica. While insect larvae have been proposed as a source of biofuel, we are not suggesting that formic acid is a potential biofuel produced from ants.

Formic acid (FA) is the simplest carboxylic acid with the structure HOCHO and pK of ~4, much like the pK of its next homologue, acetic acid (also known as “vinegar”). After its discovery FA was found useful for tanning leathers and then as a bactericide. The current world production of 500,000 tons/year is largely accomplished in Europe.

As an nonfossil fuel, hydrogen is widely viewed as an alternative; however, hydrogen is not a liquid and thus demands significant investments in tanks for storage. Because of this storage problem, there is interest in hydrogen-containing molecules, so-called “hydrogen carriers”. Ammonia is one example of a hydrogen carrier that can be produced from hydrogen generated using renewable electricity. Such fuels produced from renewable electricity are sometimes called “e-fuels”. Methanol, another popular candidate for renewable fuel, is made from H₂ and CO₂. More recently, FA has been identified as a hydrogen carrier. Renewable hydrogen can be combined with CO₂ to produce the e-fuel, formic acid. One liter of formic acid has the same amount of hydrogen as in a compressed hydrogen storage tank at 700 bar. FA has been proposed as a hydrogen source for fuel cells, wherein FA undergoes a simple reaction process to produce pure H₂ and CO₂. In this paper, we ask, can formic acid be used as an e-fuel directly in an internal combustion engine?

As many combustion systems are designed for combustion of hydrocarbons in air, it is desirable to have flame speeds of new fuels be comparable to flame speeds of hydrocarbons in air. Methane has a typical flame speed of \( S_{10} = 43 \text{ cm/s} \) at atmospheric pressure and 343 K. On the other hand, formic acid blends with oxygen have low burning velocities, as shown by de Wilde and van Tiggelen. The laminar burning velocity of formic acid may be increased by blending with H₂, and as noted earlier, formic acid can be easily decomposed to H₂ and CO₂. Therefore, this paper explores the laminar burning velocities of formic acid and its mixtures with H₂ and CO₂ at various conditions.

There have been limited studies on the combustion of formic acid in flames. Most previous work has dealt with formic acid decomposition in shock tubes and flow reactors. The most recent theoretical work on formic acid was performed by Marshall and Glarborg, and they also summarized all previous literature on this fuel. The authors performed high-level quantum chemical thermochemistry and kinetic calculations...
to identify critical formic acid consumption pathways. In addition, they developed a chemical kinetic model that was validated against flame speed measurements performed by de Wilde and van Tiggelen. Given the aforementioned interest in formic acid as an e-fuel, we conducted a detailed investigation of its laminar burning velocities at various initial temperatures and equivalence ratios. To promote the viability of using formic acid in real engines, we also studied laminar premixed flames of formic acid blended with various proportions of H2 and CO2. To provide further insights into the combustion of formic acid and its mixtures with H2 we also present an updated chemical kinetic model and use it to perform reaction flux and sensitivity analyses.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

Experimental Setup. The experiments were performed in a spherical stainless steel combustion chamber, as reported in refs 13 and 14. Since both setups (PRISME and KAUST) follow similar methodologies, for the sake of conciseness, only the configuration and methodology of the PRISME vessel is discussed. The inner volume of the chamber is 4.2 L with an inner diameter of 200 mm. The outer surface of the sphere is equipped with a heater wire resistance to heat the fresh gases to a maximum initial temperature of 473 K. Experiments were carried out at an initial pressure of 0.1 MPa. Equivalence ratios in the prepared mixture were within 2 K from the desired initial temperature. Two tungsten electrodes (1 mm diameter), with a 1 mm gap, linked to a conventional capacitive discharge ignition system were used. In the present experiments, the time charge of the ignition coil was set to 3 ms, which corresponds to a discharge energy of less than 100 mJ. More details can be found concerning the device in ref 15.

To measure laminar flame speeds, the Schlieren technique was used. Optical access into the chamber was provided by two opposite and transparent windows (diameter 70 mm). A white LED lamp was used to provide continuous and incoherent light. A parallel light was obtained using a pinhole (diameter 0.8 mm), placed just in front of the LED. The optical setup is fully described in Figure 1. Instantaneous images were recorded using a Phantom v1210 high-speed video camera operating at 10 000 images/s. The temporal evolution of the expanding spherical flame was then processed. Images of 640 × 800 pixels2 were recorded with a magnification ratio of 0.11 mm/pixel. Measurements are limited to flames with a diameter greater than 6.5 mm to avoid ignition effects and lower than 25 mm. For the extrapolation, the minimum flame radius considered to avoid ignition effect was 6.5 mm, as suggested by Bradley et al.16 and validated on the PRISME setup in ref 17. The maximum radius used was 25 mm when possible. This radius corresponds to less than 1.6% of the volume of the vessel which avoids pressure increase (isobaric hypothesis) and confinement effects.18 In some cases, when cells on the flame surface appeared, this maximum radius was adapted from one case to another and decreased to before the onset of cellularities.

From image postprocessing, the temporal flame front radius evolution was obtained. Images were processed using an in-house routine after background subtraction. The stretch rate for a spherical flame is given as

$$\kappa = \left( \frac{2}{R_t} \right) S_0,$$

where

$$S_0 = \frac{dR_t}{dt}$$

is the stretched flame propagation speed and $R_t$ represents the mean flame radius, obtained from Schlieren measurement of the projected flame area. Since the flames are stretched, correlations are employed to evaluate the unstretched laminar flame speed by extrapolation to zero stretch. The KAUST vessel employs linear extrapolation

$$S_0 - S_e = L_0 \kappa,$$

where $L_0$ is the Markstein length of the burnt gas, $S_e$ is the unstretched flame speed, $S_0$ is the stretched flame speed, and $\kappa$ is the stretch rate. Both linear and nonlinear extrapolations give very similar results when the Markstein length is close to zero and there is a large monotonic speed vs stretch curve, as shown in Figure S1. The PRISME vessel employs nonlinear correlations proposed by Kelly and Law19 and Halter et al.:20

Figure 1. Schematic overview of the experimental setup used at PRISME, Université d’Orléans (left), and KAUST (right).
Yu et al.\textsuperscript{23} showed the impact of radiative heat losses on laminar burning velocity (LBV) measurement could be of importance when the LBV is lower than 20 cm/s. Lhuillier et al.\textsuperscript{22} recently showed that, for ammonia/air mixtures, the error could reach up to 50% for very low LBV values.

Experimental results are presented with error bars which represent uncertainties obtained considering errors on the radius estimation, deviation on the initial pressure and temperature, a statistical error with a 95% confidence calculated from Student’s law and the standard deviation, as well as the radiation induced error as described in ref\textsuperscript{22}. Yu et al.\textsuperscript{23} showed that radiation related uncertainty was 4% for the lowest measured flame speeds (14 – 15 cm/s at $\phi = 1.5$). In the present work, the lowest flame speed for formic acid/H$_2$ mixtures measured at KAUST is $\sim$14 cm/s. These errors were taken into account into the uncertainty calculation and added onto the positive side of the uncertainty bar in the LBV results.

**Chemical Kinetic Modeling.** Detailed chemical kinetic modeling was performed to predict the laminar burning velocity of HOCHO and its mixtures with H$_2$ and CO$_2$. The present work utilized AramcoMech 2.0\textsuperscript{24–28} as the base mechanism due to its widely validated chemistry for H$_2$, CO, and C$_1$–C$_4$ hydrocarbons. The formic acid submechanism in AramcoMech 2.0 has not been rigorously developed or validated, and we found that it does not accurately reproduce the laminar burning velocity data obtained herein. To our knowledge, the most detailed kinetic study performed on formic acid is executed by Marshall and Glarborg.\textsuperscript{12} They conducted a detailed theoretical study on various HOCHO oxidation pathways and provided improved thermodynamic properties and kinetic parameters. As shown later, the mechanism proposed by Marshall and Glarborg slightly overpredicts formic acid/air burning velocities obtained here. Therefore, we updated AramcoMech 2.0 with the HOCHO submechanism from Marshall and Glarborg.\textsuperscript{12} Thermodynamic data for HOCHO and its radical intermediates, HOCO and OCHO were adopted from the sources\textsuperscript{29,30} recommended by Marshall and Glarborg.\textsuperscript{12} Their formic acid reaction submechanism and associated kinetic parameters were adopted without modification. The relevant reactions replaced in AramcoMech 2.0 are associated with formic acid unimolecular decomposition, H atom abstraction from HOCHO, and the decomposition of its radical intermediates (HOCO and OCHO). The kinetic model is available as Supporting Information. All simulations were conducted in ANSYS CHEMKIN PRO using the PREMIX module. Thermal diffusion was included with average mixture transport. Gradient (GRAD) and curvature (CURV) were set at 0.05 to ensure highly resolved flame structures, and solutions were converged at above 200 grid points.

## 3. RESULTS AND DISCUSSION

Experimental results for the laminar burning velocity (LBV) of HOCHO/air mixture are presented as a function of the equivalence ratio for two initial temperatures: 373 and 423 K in Figure 2 (left). The results show a maximum laminar burning velocity for slightly rich mixtures between $\phi = 1.1$ and $\phi = 1.2$ comparable with conventional hydrocarbon fuels. The LBV values are quite low compared to conventional hydrocarbons. For instance, stoichiometric methane/air at 1 bar, 373 K, displays a LBV of 0.53 m/s using AramcoMech 2.0. The experimental results are also compared with those of the Marshall and Glarborg model.\textsuperscript{12} The experimental results show

$$\left(\frac{S}{S_0}\right)^2 \ln \left(\frac{S}{S_0}\right) = -\frac{2L_{28}K}{S_0}$$

Using the expansion factor, the unstretched laminar burning velocity $S_{0,0}$ is calculated as

$$S_{0,0} = \sqrt{\frac{p_b}{p_u}} \rho_u$$

where $\rho_b$ and $\rho_u$ are the burned gas density and unburned mixture density, respectively, which were calculated from the EQUIL\textsuperscript{21} subroutine of CHEMKIN-PRO. For each condition, three to four tests were carried out in order to obtain averaged values and standard deviation. Results are presented with error bars which represent uncertainties obtained considering errors on the radius estimation, deviation on the initial pressure and temperature, a statistical error with a 95% confidence calculated from Student’s law and the standard deviation, as well as the radiation induced error as described in ref\textsuperscript{22}. Yu et al.\textsuperscript{23} showed the impact of radiative heat losses on laminar burning velocity (LBV) measurement could be of importance when the LBV is lower than 20 cm/s. Lhuillier et al.\textsuperscript{22} recently showed that, for ammonia/air mixtures, the error could reach up to 50% for very low LBV and 5% for LBV of about 10 cm/s. For hydrocarbon fuels, the error seems to be higher according to the work of Yu et al.\textsuperscript{23} The correlation of Yu et al. was therefore applied to estimate the error on the current PRISME data. For the lowest LBV value, i.e., 17.4 cm/s at $\phi = 1.1$ and $\phi = 1.2$ as the base mechanism due to its widely validated chemistry for H$_2$, CO, and C$_1$–C$_4$ hydrocarbons. The formic acid submechanism in AramcoMech 2.0 has not been rigorously developed or validated, and we found that it does not accurately reproduce the laminar burning velocity data obtained herein. To our knowledge, the most detailed kinetic study performed on formic acid is executed by Marshall and Glarborg.\textsuperscript{12} They conducted a detailed theoretical study on various HOCHO oxidation pathways and provided improved thermodynamic properties and kinetic parameters. As shown later, the mechanism proposed by Marshall and Glarborg slightly overpredicts formic acid/air burning velocities obtained here. Therefore, we updated AramcoMech 2.0 with the HOCHO submechanism from Marshall and Glarborg.\textsuperscript{12} Thermodynamic data for HOCHO and its radical intermediates, HOCO and OCHO were adopted from the sources\textsuperscript{29,30} recommended by Marshall and Glarborg.\textsuperscript{12} Their formic acid reaction submechanism and associated kinetic parameters were adopted without modification. The relevant reactions replaced in AramcoMech 2.0 are associated with formic acid unimolecular decomposition, H atom abstraction from HOCHO, and the decomposition of its radical intermediates (HOCO and OCHO). The kinetic model is available as Supporting Information. All simulations were conducted in ANSYS CHEMKIN PRO using the PREMIX module. Thermal diffusion was included with average mixture transport. Gradient (GRAD) and curvature (CURV) were set at 0.05 to ensure highly resolved flame structures, and solutions were converged at above 200 grid points.

### 3. RESULTS AND DISCUSSION

Experimental results for the laminar burning velocity (LBV) of HOCHO/air blend at 1 bar for two initial temperatures, 373 and 423 K. Experimental data (symbols) from and simulations with present model and that from Marshall and Glarborg.\textsuperscript{12} (right) Comparison of the present model with data for HOCHO/O$_2$/N$_2$ at 433 K and various levels of N$_2$ dilution. Experimental data from de Wilde and van Tiggelen\textsuperscript{6} simulations (lines) with present model.
good agreement with the mechanism especially at 423 K. The mechanism of Marshall and Glarborg was validated using the data of de Wilde and van Tiggelen. Those data were not obtained at 433 K and with air as oxidiser but were obtained with high oxygen content (minimum 76 vol % O₂) leading to higher values: between 65 and 85 cm/s for the conditions investigated in ref 6. A higher discrepancy is observed between the Marshall and Glarborg mechanism and the present experiments at 373 K, up to 5 cm/s in the worst case.

At 423 K, the model developed in this work reproduces the present experimental measurements within the uncertainty bounds at all conditions except the richest equivalence ratio, at which point the model is within 10% of the experimental measurement. The position of the maximum burning velocity at 423 K in both experiments and simulations is between \( \phi = 1.1 \) and \( \phi = 1.2 \). At 373 K, the proposed model reproduces the experimental measurements at lean conditions; however, at stoichiometric and rich conditions, the model shows up to 15% discrepancy with the experimental measurements (less if the error bars are considered). The position of maximum burning velocity at 373 K is difficult to ascertain from the measurements given the uncertainties; however, both experiments and simulations show a relatively small variation in burning velocity (within 1 cm/s) from \( \phi = 1 \) to \( \phi = 1.3 \).

Figure 2 also compares the present model against measurements by de Wilde and van Tiggelen obtained in high \( \text{O}_2 \) content mixtures with \( \text{N}_2 \). The present model accurately reproduces the location of peak LBV (near \( \phi = 0.8 \)) at all conditions, as well as measurements with 12% \( \text{N}_2 \) dilution. However, the model overpredicts data acquired under high \( \text{N}_2 \) dilutions. Similar levels of agreement were observed by Marshall and Glarborg using their model.1 Given that the measurements by de Wilde and van Tiggelen were acquired prior to many modern developments in LBV measurements, we did not tune the model to match those experiments.

Considering formic acid as a potential fuel, its low LBV is a drawback for premixed combustion application such as gas turbines or spark-ignition engines. As it is currently done with other low reactivity fuels, such as ammonia31,32 another fuel such as hydrogen or methane could be used as a reactivity promoter. Formic acid can be produced from \( \text{H}_2 \) and \( \text{CO}_2 \) with a maximum efficiency of 42% currently,33 and formic acid can be catalytically decomposed back to \( \text{H}_2 \) and \( \text{CO}_2 \). Therefore, it is interesting to study \( \text{H}_2/\text{CO}_2/\text{HOCHO} \) blend as a potential candidate for premixed combustion. The following blends were tested and considered as fuels: 25% \( \text{HOCHO}/37.5\% \text{H}_2/37.5\% \text{CO}_2 \), 30% \( \text{HOCHO}/35\% \text{H}_2/35\% \text{CO}_2 \), and 35% \( \text{HOCHO}/32.5\% \text{H}_2/32.5\% \text{CO}_2 \). The ratios were selected from the first round of simulations to obtain LBV values similar to those for methane/air mixtures. Moreover, considering these blends as potential fuels for spark-ignition engines, unburned formic acid at the exhaust is unacceptable. Therefore, the experiments at PRISME focused on lean equivalence ratios ranging from 0.5 to 0.9 to obtain maximum combustion efficiency and to be in a low \( \text{NO}_x \) region for future applications. For comparisons, experiments at KAUST have been conducted for 10% \( \text{H}_2/90\% \text{HOCHO} \) mixture as the fuel at 358 K and lean to rich conditions. Figure 3 presents LBV values obtained from experiments and simulations with the proposed model for the studied blends.

Figure 3 shows that mixing 90% \( \text{HOCHO} \) with 10% \( \text{H}_2 \) and burning in air increases the LBV compared to pure \( \text{HOCHO} \), even though the former were performed at lower unburnt gas temperatures. The proposed kinetic model is able to predict the effect of \( \text{H}_2 \) blending on LBV. Comparisons against predictions made by the Marshall and Glarborg model are shown in Figure S2. Furthermore, blending \( \text{H}_2 \) and \( \text{CO}_2 \), which are the complete decomposition products of \( \text{HOCHO} \), can extend the flammability toward leaner mixtures. In addition, it enables an increase in the LBV to ∼40 cm/s at an equivalence ratio of 0.9, which is comparable to the \( \text{CH}_4/\text{air} \) LBV at similar conditions. The LBV displays similar values for very lean mixtures regardless of hydrogen content, which can be explained by measurement difficulties in the lean flammability limit region. The proposed mechanism well predicts the LBVs of 90% \( \text{HOCHO}/10\% \text{H}_2 \) and all \( \text{HOCHO}/\text{H}_2/\text{CO}_2 \) blends compared to the present experimental work. Moreover, the differences in the three \( \text{HOCHO}/\text{H}_2/\text{CO}_2 \) blends obtained with the mechanism are in good agreement with the experiments; i.e., increasing the \( \text{H}_2 \) content increases the LBV. Finally, the shift of maximum LBV towards a richer equivalence ratio, as is observed when blending 10% hydrogen with 90% \( \text{HOCHO} \), is reproduced in simulations with the proposed mechanism.

The standard deviations are high for the 35% \( \text{HOCHO} \) blend at \( \phi = 0.76 \) and 0.83 because only two successful measurements could be obtained. For those cases, one of the experimental runs showed cellularity early in the flame development, thus preventing the images from being processed. The same happened for the 25% \( \text{HOCHO} \) blend at \( \phi = 0.51 \) where higher uncertainty is observed. As a result, having only two valid measurements of the LBV and \( \text{L}_b \) for such conditions leads to a high statistical error because the Student’s law result increases with the decreasing number of tests. Moreover, highly negative Markstein lengths cause thermodiffusive instabilities, and therefore cellularity on the flame surface at some point. To avoid those cells, the radius range usable for the extrapolation is sometimes reduced, which adds to the challenge of finding a fit under such conditions.

![Figure 3](https://dx.doi.org/10.1021/acs.energyfuels.0c00944)  
Figure 3. LBV vs equivalence ratio at 1 bar and 373 K for various \( \text{HOCHO}/\text{H}_2/\text{CO}_2/\text{air} \) blends and 358 K for 10% \( \text{H}_2/90\% \text{HOCHO}/\text{air} \) blend. Symbols are experimental data, and lines are simulations using the present model.
Since flame stretch can have a significant impact on early flame kernel development and therefore combustion phasing in spark-ignition engines, it is worth measuring the Markstein length to have an idea of the flame response to stretch and its impact on turbulent flame propagation in engines. It is especially important when H₂ is introduced since its use implies a significant change in Markstein length and Lewis number based thermodiffusive instabilities at lean equivalence ratios. Figure 4 presents the Markstein lengths obtained at 1 bar for all the studied blends at PRISME and the 10% H₂ blend tested at KAUST. The error bars presented in Figure 4 only account for standard deviations, unlike previous figures.

Markstein lengths are about 1 mm for the HOCHO/air mixture with a typical decrease as the equivalence ratio increases. This is similar in terms of absolute values and trend to conventional fossil fuels such as isooctane, as shown in ref 15. High positive values of the Markstein length lead to a decrease in flame speed when the flame stretch increases, thus making the early flame kernel propagation slow, i.e., when stretch levels are high. This is moreover representative of a stable flame without any cellularity occurring during the propagation under laminar conditions. Adding H₂ to the blend completely changes that behavior and leads to negative Markstein lengths. Negative Markstein lengths cause a decrease in flame speed as the flame propagates. The flame speed is then at its highest value in early flame kernel development when stretch levels are high, which can be beneficial in the moments right after the spark ignition. The negative Markstein length is also representative of unstable flames with cells appearing on the flame surface during laminar propagation due to thermodiffusive instabilities, as the Lewis number is low. Those instabilities make LBV measurements more difficult and lead to higher standard deviations. Finally, when hydrogen is added, the evolution of the Markstein length as a function of equivalence ratio changes: for HOCHO/H₂/CO₂ and H₂/HOCHO blends, it is opposite to pure HOCHO. Indeed, increasing the equivalence ratio increases the Markstein length for the HOCHO/H₂/CO₂ and H₂/HOCHO blends, making the flame more stable contrary to pure HOCHO. This is a typical behavior of hydrogen, which reacts to flame stretch oppositely to conventional fuels, such as isooctane. In the range of equivalence ratios studied, the Markstein lengths remain negative, but the trend suggests that values will become positive for stoichiometric and rich blends. The change of the Markstein length with hydrogen addition was already shown by Bradley et
al. with methane, especially for lean mixtures where the Lewis number and Markstein length for hydrogen are low. Bradley et al. showed that adding hydrogen to methane decreases the Markstein length almost linearly, but $L_b$ remains positive for equivalence ratio values from 1.0 to 1.2 regardless of $H_2$ content, consistent with the work of Tahtouh et al. for stoichiometric methane–air or stoichiometric isooctane–air. Bradley et al. also showed that, for $CH_4/H_2$ blends, increasing the equivalence ratio leads to an increase of the Markstein length similar to what is observed here in Figure 4. Hence, the stretch dependence of the HOCHO/H$_2$/CO$_2$ blend seems to be mainly dominated by the hydrogen response to stretch.

Another source of uncertainty in Markstein length and LBV measurement is the extrapolation used. Wu et al. showed that, to have a negligible uncertainty due to the extrapolation, the ratio $2L_{b,lin}/R_{mid}$ should lie between $-0.1$ and $0.15$. $L_{b,lin}$ is the Markstein length obtained with linear extrapolation, and $R_{mid}$ is the middle radius of the data used. There are two ways to limit the extrapolation: (i) either have a zero Markstein length blend, i.e., Lewis number close to unity, or (ii) have a large range of radii usable for the processing. Since the current blends are chosen as is, only the second condition can be modified by increasing the minimum radius used for the extrapolation, but it is still a moderate change with a quite small vessel such as the PRISME one. For the KAUST vessel, the vessel is sufficiently large such that linear extrapolation and nonlinear extrapolation provide negligible differences (see Figure S1). For the extreme Markstein length values, i.e., 1.2 and $-3.4$ mm for pure HOCHO at $\phi = 0.8$ and 25% HOCHO at $\phi = 0.51$, respectively, the extrapolation plots are presented in Figure 5 for the PRISME experiments.

For the positive Markstein length value, with the full radius range, i.e., 6.5–25 mm, the nonlinear extrapolation appears to better fit the data. The Markstein length obtained with the linear extrapolation is about 3.56 mm leading to a value of 0.45 for the criterion of Wu et al., which is too high. To have a better fit of the data with the linear extrapolation, the minimum radius was increased up to 11.7 mm leading to values of 2.5 mm and 0.27 for the Markstein length and Wu’s criterion, respectively. The change in the unstretched flame speed obtained with the linear extrapolation when the minimum radius is changed is about 9% (from 1.08 to 0.99 m/s). The nonlinear extrapolation is much less sensitive to the radius range. According to the work of Wu et al. with $H_2$, for $2L_{b,lin}/R_{mid} = 0.27$, the linear extrapolation leads to an underprediction of about 5% on the unstretched flame speed whereas it is about 10% with the nonlinear extrapolation. For the negative Markstein length values, i.e., $-3.4$ and $-1.25$ mm, with the nonlinear and linear extrapolation, respectively, the criterion is equal to $-0.17$ (7.5 mm < $R_f$ < 22 mm). However, a 17% difference can be observed on the unstretched flame speed values between the two correlations. In this case, the nonlinear one is preferred since the linear overpredicts the unstretched flame speed according to the paper of Wu et al. In any case, it can be seen that the criterion suggested by Wu et al. to limit the extrapolation error is obtained for $L_b$ between $-0.3$ and 1 mm, which is valid for most of our data for pure HOCHO and for the stoichiometric to rich HOCHO/H$_2$ blends, but it cannot be reached for the HOCHO/H$_2$/CO$_2$ blend. In those cases, the nonlinear extrapolation is preferred since the error will be less than with the linear extrapolation, thus justifying the use of this model. Nonetheless, this can still result in a 25% overprediction of the unstretched flame speed according to Wu et al. An improvement for the current data could be to use the nonlinear model with three fitting parameters proposed by Wu et al. as follows:

$$\frac{S_f}{S_0} = 1 - \frac{2L_{b}}{R_f} + \frac{C}{R_f^2}$$

with $C$ a constant to be determined.

Reaction path flux analysis was conducted for HOCHO/air and 25% HOCHO/37.5% H$_2$/37.5% CO$_2$/air mixtures at 1 bar, 373 K, and stoichiometric conditions. Figure 6 shows the consumption of HOCHO and its intermediates at a flame position corresponding to 75% of the HOCHO consumed. This corresponds to a temperature of ~1250 K in the HOCHO/air flame and ~1380 K 25% HOCHO/37.5% H$_2$/37.5% CO$_2$/air. In both flames, HOCHO is mainly consumed via H atom abstraction by OH, H, and O radicals. H-abstraction from the C atom is the dominant route leading to HOCCO radical. A small percentage of HOCHO is consumed to form OCHO radical, which rapidly and exclusively decomposes to form CO$_2$ + H. The HOCCO radical, being the predominant intermediate, is consumed differently in the pure HOCHO and H$_2$ blended flames. In the pure HOCHO flame, HOCCO mainly decomposes via OH loss to produce CO, which subsequently reacts with OH radicals to produce CO$_2$ + H. The same reaction is important in H$_2$ blended flames, albeit HOCCO also reacts more with H radicals to produce CO and H$_2$O. In the pure HOCHO flame, HOCCO also reacts with O$_2$ to produce CO$_2$ + HO$_2$ directly, but this reaction is less important in the H$_2$ blended flame. In summary, the primary difference in the two flames appears to be in the role of H atoms in the H$_2$ blended flame in producing more CO. Increasing CO concentrations then contribute to higher flame speeds due to the largely exothermic CO + OH = CO$_2$ + H reaction.

To better understand the role of specific reactions and species heat of formation, a sensitivity analysis was conducted for HOCHO/air mixtures at 373 K, 1 bar, stoichiometric conditions, and position corresponding to 75% of fuel consumed. Black text denotes percentage flux for HOCHO/air mixtures, while gray italicized text corresponds to 25% HOCHO/37.5% H$_2$/37.5% CO$_2$/air mixtures.
The formation CO₂, CO, H, OH, and HOCHO are important in reaction rate). The sensitivity analysis also shows that heats of analysis, and heat of formation sensitivity (via the reverse intermediates (as well as the same speed because, as shown in the flame speed) is sensitive to both forward reaction rates, indicated by the reaction rate sensitivity analysis, and heat of formation sensitivity (via the reverse reaction rate). The sensitivity analysis also shows that heats of formation CO₂, CO, H, OH, and HOCHO are important in controlling the concentrations of fuel and important intermediates. The heats of formation for CO₂, CO, H, OH, and HOCHO are well-defined. However, those of HOCHO and OCHO have larger uncertainties and should be the focus of more refined theoretical and experimental studies. The HOCHO heat of formation is more important in determining H and OH radical concentrations and flame speed because, as shown in the flux analysis, HOCHO is primarily consumed to form HOCHO while OCHO is the less important intermediate.

4. CONCLUSIONS

The combustion of formic acid and its mixtures with hydrogen and carbon dioxide in laminar premixed flames was studied across a range of conditions to obtain laminar burning velocities and Markstein lengths. Experimental results showed that formic acid/air mixture show significantly lower burning velocities compared to typical hydrocarbon/air mixtures. Formic acid can be readily decomposed to produce H₂ and CO₂, and experiments showed that H₂ addition could significantly increase burning velocities. As little as 32.5% H₂ addition (with equal parts of CO₂) to formic acid can achieve burning velocities similar to those of methane/air mixtures, thereby making the mixtures suitable as engine fuel. Different trends in Markstein lengths versus equivalence ratio for formic acid and formic acid/H₂ mixtures were observed, and these could be attributed to well-known mechanisms of hydrogen response to stretch.

A modified detailed kinetic model was presented to predict laminar burning velocities by combining high fidelity kinetic models for formic acid and small hydrocarbon fuels. The proposed model is able to reproduce burning velocities for formic acid/air mixtures and blends containing H₂ and CO₂, albeit some discrepancies were observed. Reaction path analysis showed the importance of the HOCO radical intermediate in formic acid combustion, which decomposes to CO and OH; CO then oxidizes to CO₂. Adding H₂ to formic acid accelerates the burning velocity by creating more H radicals that improve conversion of HOCO radical to CO. Sensitivity analysis showed the importance of HOCO related reactions in governing flame structure and the enthalpy of formation of HOCO radicals in controlling the small radical pool.

This study provides a foundation for future experimental and kinetic modeling studies on the combustion of formic acid and its mixtures with H₂ and CO₂. The proposed kinetic model should be compared against other experimental data, such as ignition delay times and products species distribution, in order to refine the thermochemical and kinetic parameters. The research findings presented in this work can help in the design of engines and turbines operating on formic acid and its mixtures with hydrogen.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.0c00944.

Flame speed vs stretch rate for KAUST experiments; LBV vs equivalence ratio for HOCHO/H₂/CO₂/air and 10% H₂/90% HOCHO/air blends (PDF)

Kinetic model including thermodynamic, mechanism, and transport files (ZIP)

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Laminar burning velocities at elevated pressures for gasoline and Formic Acid and Alcohols.

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