The effect of impurities on syngas combustion

(Full-Length Article)

ACCEPTED SUBMISSION TO COMBUSTION AND FLAME

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ABSTRACT

The effects of chemical impurities on the combustion of syngas were investigated, focusing on CH₄, a common component of syngas, and trimethylsilanol (TMS), an unstudied impurity related to those common to landfill-based syngas. Ignition properties were systematically investigated at high-pressure low-temperature conditions relevant to gas turbine combustor operation using the University of Michigan Rapid Compression Facility. Pressure time history measurements and high-speed imaging of the ignition process in this facility were used to determine auto-ignition delay times and observe ignition behaviors. The four simulated syngas mixtures used were (1) pure syngas: 30% H₂, 70% CO fuel volume, (2) syngas with CH₄: 27% H₂, 67% CO, 6% CH₄, (3 & 4) pure syngas with 10 or 100 ppm TMS, all with fuel-to-O₂ equivalence ratios (ϕ) of 0.1 at air dilution (i.e. molar O₂ to inert gas ratio of 1:3.76), and N₂ as the primary diluent gas. The pressures after compression were 5 & 15 atm with temperatures of ~1010 – 1110 K respectively. The results uniquely illustrated the occurrence of two-step ignition behavior at higher pressures, with two distinct regions of heat release and pressure rise. First and second auto-ignition delay times were therefore defined and interestingly the times were affected differently by the addition of impurities. The addition of CH₄ consistently increased auto-ignition delay times up to 40% at 15 atm, while increasing delay times at 5 atm by up to a factor of three. Conversely, the addition of 10 ppm TMS impurity addition caused a consistent decrease of ~ 10-30% delay times at 15 atm with insignificant impact at 5 atm, and 100 ppm TMS impurity caused consistent decreases of 50-70% at 15 atm and 20-30% decreases at 5 atm. The marked pressure dependence of the auto-ignition delay time, typical for syngas at these conditions, was virtually eliminated for the 100 ppm TMS mixture. Kinetic modeling suggests that the promoting effects of TMS are related to enhanced consumption and/or reduced production of HO₂. The impact of TMS is remarkably similar to that for SiH₄ in pure H₂, suggesting a possible trend for poorly understood Si-based species to promote auto-ignition in syngas and hydrogen mixtures.

KEYWORDS: Syngas; Impurity; Trimethylsilanol; Methane; Rapid compression facility

1. INTRODUCTION

Synthesized gas, or syngas, is a fuel mixture composed primarily of hydrogen and carbon monoxide, which can be produced via gasification or decomposition of carbonaceous feedstock such as coal, biomass, or landfill wastes. This fuel can be used directly in transportation or stationary combustion devices, enabling both a diversification of fuel sources and a reduction in pollutant emissions such as SO_x , NO_x , particulate matter, and heavy metals [1]. As this is a high-hydrogen-content fuel, increased NO_x emission is a concern and the application of abatement schemes focusing on low-temperature, lean, and/or pre-mixed conditions are currently under strong consideration, e.g. dry low- NO_x strategies in gas turbines and homogeneous charge compression ignition in internal combustion engines [2], [3]. Given that the performance and safety of these combustion schemes are highly dependent on the chemical kinetics of fuel oxidation, it is imperative that these kinetics be well understood at relevant combustion device conditions ($P \sim 1\text{--}40$ atm, $T < 1100$ K) for air-dilute mixtures over a range of equivalence ratios [4]–[6]. Additionally, the high variability in syngas fuel composition and its potential effects on syngas combustion must be considered, as diverse combinations of H_2 , CO , CH_4 , CO_2 , N_2 , and other trace species such as Si, N, and S-based compounds are known to exist in real mixtures [7]–[9]. This variation is detailed in Table 1, which illustrates typical syngas composition in real industrial applications. As indicated by Glarborg [10], these impurities have the potential to drastically alter the reactivity and dominant chemical kinetic pathways of the fuel oxidation process.

Table 1. Typical Syngas Composition [7]–[9], [11]

Component	% by Volume
H ₂	25-30
CO	30-60
CO ₂	5-15
H ₂ O	2-30
CH ₄	0-5
N ₂	0-4
Ar, N ₂ , H ₂ S, COS, NH ₃ , Ash	0-1
Trace Impurities (Fe, Cl, Si - species, Metals, etc.)	< 100 ppm

While the chemical kinetics of basic syngas mixtures (hydrogen and carbon monoxide only) have been well studied, see Chaos and Dryer [4] and the references therein, there are few experimental investigations on the effects of impurities and constituent variation on the combustion of syngas mixtures. Mathieu et al. [12] measured the effects of variations in CH₄, CO₂, H₂O, and NH₃ content on auto-ignition delay using a shock tube at ~98% Ar dilution, $\phi = 0.5$, $P = 2\text{--}32$ atm, $T = \sim 960\text{--}1860$ K. The results indicated that the addition of up to 0.16% CO₂, 0.22% H₂O, or 0.02% NH₃ by total mixture volume had negligible effect at all conditions, while the addition of up to 0.08% CH₄ increased the auto-ignition delay time by up to an order of magnitude. Additionally, Mathieu et al. [13] investigated the effects of several compounds on syngas auto-ignition delay time using numerical methods, considering the addition of up to 15% CH₄, 1.7% C₂H₆, 5.3% C₂H₄, 0.7% C₂H₂, 21.8% H₂O, and 15% CO₂ by total fuel volume for mixtures at air-dilution, $\phi = 0.5$ and 1.0, $P = 1\text{--}35$ atm, $T = 900 - 1400$ K. The results of this work indicated that for all hydrocarbon (HC) species except C₂H₂ an increase in the auto-ignition delay time by a factor of two or more is expected, with the most significant magnitude change for $T > 1000$ K. Gersen et al. [14] measured the effects of variations in H₂, CO, and CH₄ content on auto-ignition delay times using a rapid compression machine at approximately air-dilution, $\phi = 0.5$ and 1.0, $P = \sim 20\text{--}80$ bar, $T = \sim 900\text{--}1100$ K. The mole fraction of CH₄ in the

fuel was varied from 0 to 1, for H_2 from 0 to 1, and for CH_4 from 0 to 0.5. The results showed that while the relative concentration of CO had minimal effect, increasing the concentration of H_2 significantly decreased auto-ignition delay time and increasing the concentration of CH_4 significantly increased this time at all conditions.

In addition to these studies, the effects of impurities on the combustion of pure hydrogen have been evaluated for several compounds. As syngas combustion chemistry is dominated by hydrogen kinetic pathways [4], it is likely that effects similar to these would also be observed for syngas mixtures. Mueller et al. [15] measured the effects of NO and NO_2 addition to pure hydrogen fuel on species mole fraction profiles in a flow reactor at $\sim 1\%$ fuel dilution, $\phi = 1-2$, $P = \sim 0.5-14$ atm, $T = \sim 750-850$ K. The experimental results, as well as those from subsequent kinetic modeling, illustrated a promoting effect of both NO and NO_2 , with order of magnitude decreases in “characteristic reaction times” predicted for 10-1000 ppm concentrations. Mathieu et al. [16] studied the effects of up to 1600 ppm H_2S addition by total mixture volume on auto-ignition delay times in a shock tube at $\sim 98\%$ Ar dilution, $\phi = 0.5$, $P = 2-35$ atm, $T = \sim 960-1860$ K. The findings of that study illustrated an inhibiting effect, with increases in auto-ignition delay time of up to a factor of six. Petersen et al. [17] measured the effects of up to 0.046% Silane (SiH_4) addition by total mixture volume on the auto-ignition delay times of pure hydrogen in a shock tube at $\sim 98\%$ Ar dilution, $\phi = 1.0$, $P = \sim 1$ atm, $T = \sim 1000-2250$ K. The results indicate that the addition of $\sim 1\%$ SiH_4 to the fuel volume led to decreases in the auto-ignition delay time by a factor of two or more. This finding is in agreement with the previous study by McClain et al. [18] which indicated that increasing concentration of SiH_4 in an H_2 mixture significantly decreased auto-ignition delay times in a shock tube with $\sim$ air-dilution, $\phi = 1.0$ and 0.5, for $P = \sim 1.5$ atm and $T = 800-1050$ K.

Overall, previous studies of the effects of impurities on syngas and hydrogen combustion are limited to a select few species and the results indicate that different species indeed yield varying ignition promoting and inhibiting effects. While the effects of an individual impurity vary, it is probable that impurities consisting of compounds with similar structures may lead to similar effects. This hypothesis is supported by the almost universal ignition inhibiting behavior of similar HC species, illustrated by the experimental and computational work of Mathieu et al. discussed above. With this in mind, the significant promoting effect of SiH_4 in H_2 mixtures is particularly interesting, considering the substantial and increasing concentrations of organic Si compounds in syngas derived from waste (landfills, waste digesters, or water treatment facilities) [9], [19]. As detailed in Rasi et al. [9] and Pierce et al. [20] syngas from these sources contains both silanol $\{\dots\text{Si-OH}\}$ and siloxane $\{\dots\text{Si-O-Si}\dots\}$ species at up to 10-100 ppm concentrations. Common compounds include trimethylsilanol and decamethylcyclopentasiloxane, which make up a majority of the organic Si content within syngas from waste sources [9]. While the fouling tendencies of these and other organic Si species in combustion devices is well documented [19], [20], their effect on combustion chemistry has not been investigated in any capacity. Considering the significant ignition promoting effects observed for a chemically similar compound, i.e. SiH_4 , and the increasing concentrations of Si-based species in syngas, this lack of knowledge presents a significant barrier to the safe and effective implementation of this fuel.

The objective of the current study was to advance the understanding of the effects of impurities on the chemical kinetics of syngas oxidation, focusing on CH_4 and trimethylsilanol (TMS) impurities at thermodynamic and mixture conditions relevant to practical device operation. This objective was accomplished through an experimental investigation of auto-ignition delay times at lean, low-temperature, high-pressure conditions, using the University of

Michigan Rapid Compression Facility (UM-RCF). Uniquely, high-speed imaging was utilized for each experiment, ensuring that only ideal homogeneous ignition behaviors were exhibited for the data reported here. This important diagnostic enabled testing at lower temperatures and pressures not possible in previous experimental studies by other investigators, thereby expanding knowledge of impurity effects to more practical conditions. The auto-ignition delay time and pressure time history measurements were compared to predictions made using typical zero-dimensional homogeneous reactor ignition modeling and the formaldehyde oxidation mechanism of Li et al. [21] (Li 2007 mechanism), used frequently to successfully predict syngas combustion [4], [12], [22]. This model was then used to interpret and analyze observed pressure time histories and impurity effects, in order to describe behavior trends and connect these with potential underlying chemical kinetic pathways.

2. METHODS

2.1 Experimental Methods

Ignition experiments were conducted for realistic syngas mixtures with fuel-to-oxygen equivalence ratio of $\phi = 0.1$ and were air-dilute with N_2 , i.e. molar O_2 to inert gas ratio of 1:3.76. In some cases, small amounts of the N_2 diluent gas were replaced by Ar and/or CO_2 to modify the test temperature. Four fuel mixtures were used, (1) pure syngas: 30% H_2 , 70% CO fuel volume, (2) syngas with CH_4 : 27% H_2 , 67% CO, 6% CH_4 , (3) pure syngas with 10 ppm TMS, and (4) pure syngas with 100 ppm TMS. Mixtures were designed to represent lean syngas mixtures used in the power industry while spanning typical CH_4 concentrations [1], [11] and typical TMS impurity concentrations observed by Rasi et al. [9] (~ 5 ppm). Considering the upward trend in organic Si species in waste-based syngas reported by Rasi et al.

[9], the mixture containing 100 ppm TMS was selected to represent potential future concentrations. Ignition experiments were conducted at 5 and 15 atm for the broadest range of temperatures allowable in the UM-RCF for these mixtures (~ 1010 - 1110 K, based on experimental test times and associated uncertainties). While it was desirable to increase the equivalence ratio beyond the value chosen here, $\phi = 0.1$, it was not possible to achieve homogeneous ignition behavior at the thermodynamic conditions of interest for higher values of ϕ . Please see Mansfield and Wooldridge [22] for a discussion of the state and syngas mixture conditions associated with homogeneous versus inhomogeneous ignition. A detailed tabulation of the gas mixture composition and thermodynamic state corresponding to each auto-ignition delay time measurement is given in the Supplemental Material section.

Regarding the experimental apparatus, the UM-RCF is designed to create a gas volume with uniform thermodynamic conditions through an isentropic compression process. A detailed description of the UM-RCF and results of studies characterizing its performance can be found in Donovan et al. [23] and He et al. [24]. Briefly, the apparatus consists of a long cylinder, the Driven Section, in which a gas mixture is rapidly compressed by the motion of a free piston (Sabot). Prior to compression, the test volume is evacuated with a pump and then filled with a specific test gas mixture. Upon firing, the Sabot travels the length of the Driven Section compressing the test gas mixture into the Test Section – a small cylindrical volume located at the end of the Driven Section (~ 50 mm length and 50 mm diameter). As the Sabot reaches its final position near the Test Section, the Sabot achieves an annular interference fit, thereby sealing the test gas mixture in the Test Section. At this point, the Test Section is filled with a uniform and isentropically compressed test gas mixture at the desired initial thermodynamic condition. For this study, the Test Section was instrumented with a piezoelectric transducer (6125B Kistler,

Amherst, NY) and charge amplifier (5010 Kistler, Amherst, NY) for pressure measurements, and a transparent polycarbonate end-wall to permit high-speed imaging of the ignition process. During each experiment the pressure time history was recorded using the pressure transducer at 100 kHz sampling frequency. The uncertainty in the pressure measurements is estimated as $\leq 1\%$ (~ 0.1 atm) considering both the signal-to-noise ratio in the post-ignition pressure time history data and the non-linearity limits defined by the manufacturer during the calibration process. High-speed color imaging was recorded using a digital video camera (V711-8G-MAG-C, Vision Research, Phantom) with a Navitar 50mm lens (F0.95), a Hoya 62 mm lens (+2 zoom), and a Hoya 62 mm UV(0) filter. Video sequences were recorded at 25,000 frames/second with the CMOS array with resolution of 512 x 512 pixels, resulting in an exposure time of 39.3 μ s.

All test gas mixtures were made using a dedicated stainless steel tank and the mixture composition was determined by measurement of the relative partial pressures of the components. After filling, the tank was continuously stirred by an internal mechanism and was left to mix for at least one hour before use. Error in the mixture composition is assumed to be negligible and have negligible effect on the ignition results, considering ~ 80 -95% (mole basis) of the mixture is comprised of N_2 and O_2 .

2.2 Computational Methods

Auto-ignition delay time and pressure time history predictions were made using the constant volume adiabatic zero-dimensional homogeneous reactor model in the CHEMKIN software suite [25] with the Li 2007 chemical kinetic mechanism. This mechanism was used given previous success in predicting syngas ignition behavior [4], [21], [22] and because it includes CH_4 oxidation chemistry. Using this auto-ignition model, a corresponding auto-ignition

delay time prediction was calculated for each ignition experiment in this study using the initial thermodynamic condition and mixture composition of the experiments. The auto-ignition delay time from the model predictions was defined as the time from the start of the calculation to the time when $dT(t)/dt$ was maximized. In some cases two inflection points were predicted in the temperature time history, indicating two “steps” of energy release during ignition. The occurrence of two-step auto-ignition corresponds well to the experimental observations and is discussed in detail below. Important to note is that TMS is not included in the Li 2007 mechanism and the authors are aware of no oxidation model which includes this species and associated combustion products. Therefore auto-ignition delay time predictions are presented only for experiments which used the pure syngas or syngas with CH_4 mixtures. For each prediction, quantified uncertainty bounds were calculated using the known uncertainty in the “A-factor” of the Arrhenius reaction rates for the four most sensitive reactions, $CO + O_2 = CO_2 + O$ (R21), $HO_2 + H = H_2 + O_2$ (R10), $H + O_2 = H + OH$ (R1) and $H + O_2 (+M) = HO_2 (+M)$ (R9). These were identified using OH sensitivity analysis conducted in the CHEMKIN software suite for the pure syngas mixture at $P = 15$ atm, and $T = 1066$ K. The results of the sensitivity analysis and the rate coefficients used are listed in Supplemental Material.

3. RESULTS

For each experiment in the UM-RCF, a pressure time history and a high-speed imaging video were recorded, allowing for the determination of auto-ignition delay times and direct observation of the auto-ignition behavior. A typical pressure time history during an ignition experiment for initial pressures of 15 and 5 atm can be seen in Figs. 1 and 2, respectively. Similar trends are observed for both experiments. The pressure initially increases during the compression stroke until the Sabot is seated at the end-of-compression (EOC) event, followed by

a slight decrease in pressure due to heat transfer from the test gas volume into the cool Test Section walls, followed by a large and rapid increase in pressure during the ignition. For each experiment, the time and pressure were noted at the three distinct events: end-of-compression, minimum pressure ($P_{\min}$), and maximum pressure ($P_{\max}$), highlighted in Fig. 1. After filtering the pressure time history with a 75-point smoothing algorithm to reduce signal noise, the pressure and time value for each event were defined mathematically as a local maximum or minimum respectively. The pressure data ($P(t)$) between $P_{\min}$ and $P_{\max}$ was then filtered a second time with a 100-point smoothing algorithm to further reduce signal noise, and the numerical derivative of the pressure time history ($dP(t)/dt$) was calculated using a center differencing scheme.

For each auto-ignition experiment a thermodynamic state was assigned representing the unburned isothermal isobaric condition at which the experiment was conducted. The gas temperature within the Test Section was calculated using thermodynamic relations as this temperature was not measured directly. As suggested by Lee and Hochgreb [26] and experimentally verified by Donovan et al. [23], the initial compression stroke and the post-compression expansion of the adiabatic core region in the UM-RCF are well represented as an isentropic compression process. Therefore, the initial uncompressed thermodynamic conditions were used in conjunction with isentropic state relations to calculate the temperature at both EOC and $P_{\min}$. Propagation of the pressure measurement uncertainty of $\leq 1\%$ through the isentropic state relations yields an uncertainty of $\leq 0.4\%$ in the assigned temperature (~ 5 K). In most cases, there was no appreciable decrease in temperature between the EOC event and the ignition event (i.e. < 10 K change from EOC to $P_{\min}$), and so the EOC thermodynamic state represented the experiment well, and was assigned to the auto-ignition delay time measurement. For experiments with appreciable decrease in temperature (i.e. > 10 K) between EOC and $P_{\min}$, an

average thermodynamic state was assigned in order to incorporate the effects of post-compression heat transfer. The average pressure was defined mathematically as the arithmetic mean of the pressure measured from EOC to $P_{\min}$ and the average temperature was calculated thereafter assuming an isentropic expansion from the thermodynamic state at the EOC event to the average pressure. Assignment of an average state in this manner has been successfully applied in numerous past experiments using the UM-RCF for similar syngas fuels [22], [27]. As discussed in detail in Mansfield and Wooldridge [22], assignment of an average state allows for accurate incorporation of heat transfer effects while retaining critical clarity in reporting, vastly improving the archival value of the results as compared to the assignment of the EOC condition only.

For experiments with an initial pressure of 15 atm, seen in Fig. 1, trends in the dP/dt time history exhibited two peaks for all mixtures; one corresponding to each “step” of pressure rise during the ignition event. As evidenced, each step represents a region of rapid pressure rise and the two steps observed are separated by a region with a reduced rate of pressure rise. Two ignition delay times were therefore determined for each experiment that exhibited these features ($\tau_{i,1}$ and $\tau_{i,2}$) as the time from EOC to each peak in the dP/dt time history. The definitions are illustrated in Fig. 1. For experiments with an initial pressure of 5 atm, as presented in Fig. 2, a single peak in dP/dt was observed for all mixtures and correspondingly one ignition delay time, $\tau_{i,2}$, was determined from each of these experiments. The most significant source of uncertainty associated with these auto-ignition delay time measurements is from the selection of the smoothing algorithm in the data filtering process. Uncertainty for each measurement was quantified by varying the number of points included in the initial filtering algorithm by $\pm 50\%$ and defining bounds for each measurement which spanned the resulting range of auto-ignition

delay times calculated. In the vast majority of cases the uncertainty in the measured auto-ignition delay time was $< 1\%$; though, in a few select cases 20- 35% uncertainty was observed, likely the result of a convolution of the auto-ignition event with an artifact in the pressure time history. Uncertainty bounds in the assigned temperature values were also calculated in this manner, as variation in the smoothing algorithm parameters affects the selection of key pressure values (EOC , P_{min} , P_{max}) used to calculate the temperature. While in most cases the temperature uncertainty was less than the previously defined value of ~ 5 K, in certain cases the uncertainty exceeded this value. A tabulated list of all experimental results, including calculated uncertainty bounds for the auto-ignition delay time measurements and assigned temperatures, is provided in the Supplemental Material section.

A frame from the typical high-speed imaging results of chemilluminescence during syngas auto-ignition is shown in Fig. 3. As seen, homogeneous ignition is indicated by the spatial uniformity of the chemilluminescence emission. For each experiment the high-speed imaging results were reviewed to confirm that only homogeneous ignition occurred. This ensured that all characteristics of the pressure time history correspond to global phenomena (chemical kinetics and heat transfer), which are well represented by a zero-dimensional homogeneous reactor model. As illustrated in detail by Mansfield and Wooldridge [22], the effects of localized ignition phenomena can significantly impact the accurate interpretation of pressure time history results for syngas fuel and so avoiding these behaviors was critical in the present work.

3.1 Auto-ignition delay times at 5 and 15 atm

Fig. 4a and b illustrate the auto-ignition delay time measurement results for the second ($\tau_{i,2}$) and first ($\tau_{i,1}$) steps of the ignition at 15 atm. Overall the results for both steps illustrate excellent repeatability and consistent trends throughout the temperature range evaluated. The data demonstrate TMS can be added to the syngas mixtures in a controlled and consistent manner in the present experimental system, an important verification considering that this compound has not been tested in any known previous combustion experiment. The effects of CH_4 and TMS impurity addition are in trend wise agreement between the first and second auto-ignition delay times, generally with CH_4 inhibiting and TMS promoting ignition, though the magnitude of the impact is more pronounced for $\tau_{i,2}$. The generally observed inhibiting effects for the syngas with CH_4 mixture are in agreement with previous findings by Gersen et al. [14] and Mathieu et al. [12] who also observed this outcome.

Regarding the results for $\tau_{i,2}$ shown in Fig. 4a, it is apparent that the addition of CH_4 consistently increases the auto-ignition delay time relative to the pure syngas mixtures by $\sim 40\%$. Conversely, the addition of TMS causes a decrease in the auto-ignition delay times, with magnitude dependent on both the concentration and the initial temperature. For 10 ppm TMS addition, significant effects are only observed at $T > 1060$ K, at which point the auto-ignition delay time is reduced by $\sim 30\%$. For 100 ppm TMS addition, there is a drastic impact on the measurements, with consistent 50-70% decrease in the auto-ignition delay time across all temperatures. Regarding the results for $\tau_{i,1}$ shown in Fig. 4b, it is apparent that the addition of CH_4 consistently increases the auto-ignition delay time measurement by 40-50%. Again, the addition of TMS results in a reduction in measured auto-ignition delay times; where 10 ppm addition leads to a consistent 10-30% reduction, and 100 ppm leads to a consistent 45-50% reduction. As the effect of 10 ppm and 100 ppm TMS addition was similar for $\tau_{i,1}$, but

drastically different for $\tau_{i,2}$, this suggests that the second step of the ignition process is more sensitive to this impurity. Conversely, the difference between $\tau_{i,1}$ and $\tau_{i,2}$ remains approximately constant at ~ 5 ms for both pure syngas and syngas with CH_4 across all conditions.

Fig. 5 illustrates the auto-ignition delay time measurement results ($\tau_{i,2}$) for 5 atm initial pressure. Again, the results indicate excellent repeatability and consistent trends throughout the temperature range. Recall that the uncertainty bounds of the temperature assignments are the limits of the post-processing filtering algorithm parameters. The effects of CH_4 and TMS generally agree with those at 15 atm, with CH_4 inhibiting and TMS promoting ignition, but the magnitudes of the impact differ. It is apparent that the addition of CH_4 has minimal impact below 1050 K, though at higher temperatures the auto-ignition delay time is increased by up to a factor of 3. While the apparent activation energy (the slope of the auto-ignition delay time as a function of the inverse temperature) decreases as temperature decreases for all other mixtures, the apparent activation energy for the syngas with CH_4 mixture does not change as a function of temperature. For 10 ppm TMS addition, there is no significant effect on the auto-ignition delay time; whereas for 100 ppm TMS addition, there is a consistent 20-30% decrease in the auto-ignition delay time. Interestingly, as the temperature increases to ~ 1070 K, the auto-ignition delay time appears to be increasingly less sensitive to addition of 100 ppm of TMS or CH_4 , suggesting that the effects of these impurities at these mole fraction levels are negligible at temperatures above this value. This may be the result of reductions in the magnitude of the auto-ignition delay times at these conditions, as compared to lower temperatures and higher pressures.

3.3 Pressure dependence

As demonstrated in the figures above, the effect of TMS addition on the auto-ignition delay time is highly pressure dependent, with significantly larger magnitude impact at 15 atm. Fig. 6 illustrates the auto-ignition delay time measurements for the second step of the ignition process ($\tau_{i,2}$) at both 5 and 15 atm for the pure syngas and syngas with TMS mixtures. Regarding the pressure dependence of the auto-ignition delay time, there is a dependence for the pure syngas mixture illustrated in Fig. 6, with increases in ignition delay time of up to 100% as the pressure is increased from 5 to 15 atm at the same temperature. This behavior is indeed expected as the increase in pressure corresponds to a shift to slower HO_2 and H_2O_2 dominated chemical kinetic pathways [28]. While 10 ppm TMS addition has minimal impact on this pressure dependence, it is evident that 100 ppm TMS addition reduces the pressure dependence of the auto-ignition delay time to nearly zero. As this pressure dependence is likely closely related to HO_2 and H_2O_2 dominant chemistry, this suggests that the promoting effect of TMS is related to interaction with these species.

Remarkably, similar significant reduction in both auto-ignition delay times and the pressure dependence of the auto-ignition delay time was reported by both Petersen et al. [17] and McLain et al. [18] for SiH_4 addition to pure H_2 mixtures. Jachimowski and McLain [29] postulated that this decrease in pressure dependence was due to HO_2 radical scavenging by SiH_4 , promoting H_2O_2 and subsequently OH formation, though these claims have not been evaluated experimentally.

3.4 Comparison with kinetic model predictions

As previously mentioned, predictions for auto-ignition delay times of pure syngas and syngas with CH_4 were made using the Li 2007 mechanism and the homogeneous reactor model

in CHEMKIN. For all 15 atm experiments, the kinetic model accurately predicted the existence of a two-step ignition process; whereas, for 5 atm the kinetic model predicted single step ignition in most cases, though two-step ignition in rapid succession (< 1 ms separation) was predicted for some conditions. This is not in disagreement with the measurements at 5 atm however, as the resolution of the experiment, due to the data smoothing process, is insufficient to accurately observe two ignition steps in such immediate occurrence. Typical pressure time history results (normalized by the initial pressure for clarity in the comparison) from simulations with initial conditions $P = 5$ and 15 atm, $T = 1066$ K, using the pure syngas mixture are seen in Fig. 7. These results demonstrate the relationship between the initial pressure and the time between first and second ignition steps; where for 15 atm the ignition steps are separated by ~ 4 ms, and for 5 atm, the separation is < 1 ms.

Fig. 8 and 9 illustrate the measured and predicted auto-ignition delay times for 15 and 5 atm, respectively. Recall the uncertainty bounds of the predictions are the effect of the uncertainty in the rate coefficient of reactions R21, R10, R1, and R9. As seen in Fig. 8, predictions for all temperatures, both mixtures, and both $\tau_{i,1}$ and $\tau_{i,2}$, are in excellent agreement with the measurements at 15 atm. Likewise, as illustrated in Fig. 9, predictions for both mixtures for all temperatures at 5 atm are in very close agreement with the experimental data except for the syngas with CH_4 mixture. Predictions for this mixture at temperatures below ~ 1040 K are faster than the measurements and outside the uncertainty bounds. While this may suggest error in the Li 2007 kinetic mechanism, these data correspond to the lowest temperatures and longest auto-ignition delay times, therefore it is possible that the slight disagreement is the result of more pronounced heat transfer effects not sufficiently captured by the model. Overall the evidence in Figs. 7 - 9 shows the system is well represented by the Li 2007 chemical kinetic reaction

mechanism and a homogeneous reactor physical model, importantly allowing for more the detailed chemical kinetic analysis discussed below.

4. DISCUSSION

4.1 Two-step Ignition Behavior

The experimental results of the present work illustrates the existence of a two-step ignition process for experiments with 15 atm initial pressure, embodied by two distinct regions of heat release and corresponding pressure rise. Furthermore, model predictions indicate that near 5 atm, two-step ignition is likely occurring though the steps are in such rapid succession that it is not possible to observe a separation in time experimentally. The existence of this two-step ignition behavior for syngas fuel mixtures has not been previously reported, although similar behavior is evident in the pressure time history results of Keromnes et al. [30] and Kalitan et al. [31]. As the auto-ignition delay time is often defined as the time where dP/dt is maximized, it is possible that in these and other previous studies multi-step ignition behavior was observed but only a single auto-ignition delay time was reported. Additionally, given that historical combustion experiments were conducted primarily near atmospheric pressures, according to Chaos and Dryer [4] and the references therein, it is possible that significant two-step ignition was not exhibited for a majority of these lower pressure studies.

As demonstrated above, the two-step nature of the ignition process was well predicted by the Li 2007 kinetic mechanism in the CHEMKIN reactor model. It was therefore possible to use this model in more detail, to probe trends in two-step behavior across various conditions as well as its chemical kinetic foundations. Of particular interest was the dependence of this behavior on initial pressure. Additionally, given the highly variable nature of syngas mixture composition,

understanding how this two-step ignition behavior is affected by constituent variation, e.g. the ratio of $\text{H}_2:\text{CO}$, is also important. In order to evaluate the effects of these factors, simulations were conducted for a range of initial thermodynamic state and mixture conditions. Illustrated in Fig. 10 are predicted pressure time histories for syngas mixtures with $P = 5$ and 15 atm, $T = 1066$ K, for air-dilute mixtures with $\phi = 0.1$, and variable $\text{H}_2:\text{CO}$ (molar ratio) of 1:3, 1:1, 3:1, 1:0. Note that the pressure values are normalized by the initial unburned value for comparative clarity. Considering these predictions, it is evident that the occurrence of two-step ignition behavior is strongly dependent on both the initial pressure and the molar ratio of H_2 to CO . Noticeably, significant two-step ignition behavior is not apparent at 5 atm for these conditions; however, the addition of CO does impact the rate of pressure rise during the ignition event, with increasing amounts of CO yielding lower pressure rise rates. This is in excellent agreement with the experimental findings of the present work, and indeed supports the notion that previous studies of syngas near atmospheric conditions would likely not observe two-step ignition behavior. In contrast, at 15 atm two-step ignition behavior, indicated by two distinct regions of differing rate of pressure rise, is apparent for all mixtures except pure H_2 . At this higher pressure both the relative magnitude of pressure rise from the second step and the time separation between first and second steps of the ignition process are increased with CO . Remarkably, at 15 atm and the highest CO concentration there is a marked increase in the time of energy release during both first and second steps of the ignition process as compared to the other conditions evaluated. For example, at 5 atm and $\text{H}_2:\text{CO} = 1:1$, the heat release and corresponding pressure rise from initial to final states occurs over < 1 ms; whereas, for 15 atm and $\text{H}_2:\text{CO} = 1:3$ the same relative pressure rise occurs over more than 10 ms. In a practical application, two-step heat

release and ignition behavior of this significance could have a marked impact on system performance if not appropriately considered.

The effect of equivalence ratio on two-step ignition behavior was also investigated computationally, in order to assess the impact of such behaviors at a mixture condition more directly relevant to combustor operation. Illustrated in Fig.11 are simulated pressure time histories for syngas mixtures with $P = 15$ atm, $T = 1066$ K, for air-dilute mixtures with $\phi = 0.1 - 1.0$, and $H_2:CO$ (molar ratio) of 3:1. The pressure, temperature and $H_2:CO$ conditions were selected for further study as they exhibited the most pronounced two-step behavior in Fig. 10. As in Fig. 10 the pressure values in Fig.11 are normalized by the initial unburned value for comparative clarity. It is evident that the magnitude of two-step ignition behavior is strongly related to the equivalence ratio, with pronounced separation between first and second stages for $\phi = 0.1 - 0.15$, and negligible separation for higher values. This is further support of the notion that two-step ignition behaviors were not observed in previous studies, as previous studies tended to focus on higher equivalence ratio conditions.

The relationship between two-step ignition behavior and both the initial pressure and molar ratio of $H_2:CO$ for syngas mixtures implies that these factors are important to the chemical kinetic foundations of this behavior. Regarding these foundations, it was desirable to develop an understanding of the root causes of two-step ignition behavior in syngas fuels. To accomplish this, the kinetic model was once more utilized to predict mole fraction time histories for both major and radical species during the ignition process. This simulation was conducted for the pure syngas mixture used in the present experimental work at $P = 15$ atm, $T = 1066$ K; a condition which exhibits significant two-step ignition. Illustrated in Fig. 12 are predicted mole fraction time histories at this condition, which reveal the stepped behavior in the pressure time

history is reflected in the mole fraction time histories of both major and radical species. As evidenced in Fig. 12a, during the first step of the ignition process both H_2 and CO are consumed, correspondingly forming H_2O and CO_2 . When the H_2 supply is essentially exhausted, the rate of pressure rise decreases and the rate of CO consumption remains nearly constant. This reduction in pressure rise rate is expected, as the total rate of fuel consumption decreases when H_2 is no longer significantly available. The rate of pressure rise continues at this reduced magnitude until after some time the remaining CO is rapidly consumed and a significantly larger rate of pressure rise occurs. This second rapid rise in pressure forms the second step in the pressure time history. Shown in Fig. 12b are the major radical species formed during the two-step ignition process. The simulation indicates H_2O_2 and HO_2 radicals dominate the first step of the ignition process, as predicted by Chaos et al. [28] and mentioned earlier; however, OH and O radicals dominate the second step of the ignition process.

As to the chemical kinetic foundation for two-stepped ignition behavior, the question is therefore what causes the delay in rapid CO oxidation characteristic of the second step of the ignition process? Rate-of-production analysis for CO at this condition, shown in the Supplemental Material, importantly indicates that nearly all CO is consumed via the reaction $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ (R23). This finding, in addition to the radical mole fraction time history results in Fig. 12b, suggests that the delay in rapid CO oxidation is likely related to a corresponding delay in the formation of OH . Rate-of-production analysis was therefore performed for OH , which is also shown in the Supplemental Material. Results of that analysis indicate that $\text{H}_2\text{O}_2 (+\text{M}) = \text{OH} + \text{OH} (+\text{M})$ (R15) dominates the formation of OH during the first step of the ignition process. Once the H_2 supply is nearly exhausted at the end of the first step of the ignition, the dominant formation reactions then change to primarily $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ (R1) and $\text{O} + \text{H}_2\text{O} =$

OH + OH (R4). As discussed in detail by Chaos et al. [28] and Mansfield and Wooldridge [22], $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ (R1) is in direct competition with $\text{H} + \text{O}_2 (+\text{M}) = \text{HO}_2(+\text{M})$ (R9), and the corresponding formation rate of OH is highly dependent on both pressure and temperature. Considering the competition of these reactions, as pressure is increased and/or temperature decreased the rate of OH production diminishes significantly. It is therefore likely that the pressure dependence of OH production from reactions R1 and R13 during the time after the first step of the ignition is the underlying foundation for the dependence of two-step ignition behavior on pressure. In other words, when pressure is increased, the rate of OH production after the first step of the ignition process is slowed and more time is required to build the OH radical pool to a sufficient level for rapid CO oxidation. This results in a more pronounced two-step ignition behavior as the first and second steps are separated by more time. Competition between reactions R1 and R13 can also explain the dependence of two-step ignition behavior on the $\text{H}_2\text{:CO}$ molar ratio. This ratio will affect the temperature at the end of the first step of the ignition process, with more H_2 yielding a higher temperature. The increased temperature will lead to an increased rate of OH formation and correspondingly will decrease the time between first and second steps of the ignition. Furthermore, the dependence of two-step ignition behavior on equivalence ratio can be related to these reactions, as an increase in fuel concentration will also increase the availability of OH radicals.

Overall the results of both the experimental investigation and chemical kinetic analysis of the present work illustrate an important yet often overlooked characteristic of syngas mixtures: features of multi-stage heat release. With this in mind, the method of reporting a single auto-ignition delay time, as traditionally done for syngas mixtures, misses information important to understanding the combustion kinetics of these fuels. The approach of reporting both the first

and second auto-ignition delay times is an important improvement in capturing this multi-stage behavior. Other methods for reporting could include more characteristics such as magnitude and rates of pressure rise, which may further increase the value and accuracy of similar experimental data. Note the magnitude of the effects of multi-stage heat release is convolved with the volume and heat transfer characteristics of the test section of the experimental apparatus. The amount of energy transferred to the test gases during the combustion process is directly affected by the amount of energy lost to the cool test section walls and/or expended in compressing the cool boundary layer gas volume. Consequently, care should be used when comparing multi-step ignition data from different facilities.

4.2 Inhibiting effect of CH₄

The experimental results of the present work illustrate a pressure dependent inhibiting effect of CH₄ on the auto-ignition of syngas, which is well predicted by the Li 2007 kinetic mechanism and the CHEMKIN reactor model. The inhibition effect and the trend in pressure dependence are both in excellent agreement with the findings by Mathieu et al. [12], who suggested that $\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$ (R49) was the primary reaction through which CH₄ inhibits syngas auto-ignition (identified using sensitivity analysis). Uniquely, experimental results in the present work indicate that while $\tau_{i,1}$ and $\tau_{i,2}$ are increased by the addition of CH₄, the magnitude of their difference is consistent with that for pure syngas. This suggests that the CH₄ acts primarily on the kinetics during the first step of the ignition at the present concentration. In order to evaluate this hypothesis, the CHEMKIN reactor model was once more utilized. Illustrated in Fig. 13 are predicted mole fraction time histories for the syngas with CH₄ mixture at $P = 15$ atm, $T = 1066$ K for the major species. Additionally, the predicted pressure

traces for both the pure syngas and syngas with CH₄ are included for comparison. As seen in the figure, the ignition proceeds in a very similar manner as predicted for pure syngas. Interestingly though, CH₄ is consumed completely along with H₂ during the first step of the ignition. Furthermore, OH rate-of-production analysis for this mixture, shown in the Supplemental Material, indicates that CH₄ scavenges OH during the first step of the ignition process via CH₄ + OH = CH₃ + H₂O (R49) and CH₂O + OH = CHO + H₂O (R38). After the first step of ignition, however, there is no major consumption of OH by CH₄ or related intermediates. The predicted pressure time history results also indeed illustrate a lengthening in the time of the first step of the ignition process by ~ 2 ms for the mixture with CH₄, though the time from the end of the first step to the second step remains approximately constant at ~ 3 ms. Therefore, the modeling results strongly support the notion that the effect of CH₄ impurity addition at this concentration is to directly increase $\tau_{i,1}$ through OH scavenging while minimally affecting the kinetics of the second step of the ignition process. The experimentally observed effect on $\tau_{i,2}$ is therefore likely the result of delayed heat release from the first step of the ignition process. It is possible that by increasing the relative concentration of CH₄ that its inhibition effects would extend to the second step of the ignition process, though that was not evaluated here. Overall these results again highlight the importance of comprehensively considering the multi-step ignition process, as impurities can affect the driving chemical kinetics of each step differently.

Comparison of predicted pressure time history results for each mixture illustrates a decrease in the maximum post-combustion pressure by ~ 0.15 atm for the mixture with CH₄. This can be explained by a reduction in the total heat of reaction (H_R) from 2.61 to 2.38 kcal/mol total mixture when changing from the pure syngas to the with CH₄ mixture. The specific heat capacity values are not significantly different between the two mixtures.

4.3 Promoting effect of TMS

As previously mentioned, no chemical kinetic mechanism currently exists which includes trimethylsilanol and the expected intermediate species during its oxidation. In order to evaluate the possible chemical kinetic foundations of the observed effects of TMS addition, a perturbation study was conducted using the CHEMKIN reactor model with a pure syngas fuel mixture. The perturbations were designed to explore the potential effects of the TMS impurity on the high pressure formation pathways of OH. Both Jachimowski and McLain [29] and Petersen et al. [17] suggested that SiH₄ disrupts the formation and/or enhances the consumption of HO₂ thus boosting OH production rates at high pressures. Given the effects of TMS closely resemble those of SiH₄ addition, it is possible that the kinetic foundations of the ignition promoting effect for TMS are related to changes in the same reaction pathways.

In the current work, two perturbations to the computational model were considered, which was conducted at $P = 5$ and 15 atm, $T = 1066$ K, for the pure syngas mixture. In the first, HO₂ consumption was boosted by increasing the A-factor of the reaction $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$ (R14) by up to 10^2 times, and in the second perturbation, HO₂ formation was inhibited by decreasing the A-factor of $\text{H} + \text{O}_2 (+ \text{M}) = \text{HO}_2 (+ \text{M})$ (R9) by up to 10^{-3} times. The ranges were chosen to encompass limiting behaviors in the predicted trends of the auto-ignition delay times. Results of the model analysis, shown in the Supplemental Material, indicate that indeed reductions in both auto-ignition delay time ($\tau_{i,2}$) and in the pressure dependence of the auto-ignition delay time can be achieved by modifying these reactions in the manner described. However, the magnitude of the decrease in the pressure dependence and the precise trends in the auto-ignition delay times observed experimentally are not well captured. This is expected

because replicating the precise trends would likely require accurate inclusion of TMS and several additional Si-based intermediate species in the chemical kinetic mechanism. While the creation of such a mechanism may improve quantitative accuracy of the prediction of auto-ignition delay time, mechanism development was beyond the scope of the present work. Regardless, the modeling results presented here are important in that they support the notion that the effect of TMS is indeed likely related to HO_2 kinetic pathways, in good qualitative agreement with previous assertions for the similar Si-based impurity, SiH_4 .

5. CONCLUSIONS

This work represents a unique investigation on the effects of common yet understudied impurities on the combustion of syngas fuel at thermodynamic conditions relevant to practical combustion devices, providing not only the first direct observations of sometimes drastic effects, but also highlighting trends in behavior that may extend beyond the specific compounds evaluated in the present work. Studies such as this are vital to the safe and effective application of real syngas or other high-hydrogen content fuels, especially when used in modern high-pressure low-temperature combustion strategies like dry low- NO_x .

The results of the present experimental work uniquely illustrate the occurrence of two-step ignition behavior at higher pressures, with two distinct regions of heat release and pressure rise. First and second auto-ignition delay times ($\tau_{i,1}$ and $\tau_{i,2}$) were therefore defined and interestingly the times were affected differently by the addition of CH_4 and TMS impurities. Modeling results suggest the occurrence and magnitude of two-step ignition behavior can be explained by highly pressure and temperature dependent OH kinetics, which can cause a delay between H_2 and CO oxidation thus creating two distinct steps in the ignition process. Trends

identified using this model illustrate that two-step ignition behavior becomes more prominent with increasing pressure, increasing relative concentration of CO, and decreasing equivalence ratio.

The addition of CH₄ consistently increased both $\tau_{i,1}$ and $\tau_{i,2}$ up to 40% at 15 atm, while increasing delay times at 5 atm by a factor of 3 only for $T < \sim 1050$ K. Model analysis suggests this inhibiting effect is due to OH scavenging primarily via the $\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$ (R49) reaction, which acts to slow the first step of the ignition process. Conversely, the addition of TMS consistently decreased the auto-ignition delay times, with the magnitude of the effect related to the TMS concentration and the initial pressure. 10 ppm TMS impurity addition caused a minimal effect on $\tau_{i,2}$ at both 5 and 15 atm and a consistent decrease of ~ 10 -30% in $\tau_{i,1}$ at 15 atm. The effect of 100 ppm TMS impurity addition was much more drastic, with consistent decreases of 50-70% in $\tau_{i,2}$ and 45-50% in $\tau_{i,1}$ at 15 atm and 20-30% reduction in $\tau_{i,2}$ at 5 atm. Furthermore, the pressure dependence of the auto-ignition delay time, typically causing up to 100% increase as pressure increased from 5 to 15 atm, was virtually eliminated for the 100 ppm TMS mixture. Kinetic modeling suggests that these ignition promoting effects are related to enhanced consumption and/or reduced production of HO₂, though the precise chemical kinetic effects cannot be resolved with existing kinetic mechanisms. The drastic effects of TMS have significant safety implications, as pronounced early ignition can lead to catastrophic failures. Furthermore, the upward trend in organic Si content in syngas mixtures and the current movement toward higher pressure combustion systems means consideration of these effects is of increasing importance.

The impact of TMS addition observed here is remarkably similar to that for SiH₄ in pure H₂ made in previous investigations. This suggests a possible trend for Si-based species to

promote auto-ignition in syngas and hydrogen mixtures. Such a trend may facilitate an extension of the findings in the present results beyond SiH₄ and TMS, to other Si-based species commonly present in syngas fuel. Important to note, however, is that this extension is limited by the lack of understanding as to the exact mechanism for ignition promotion. Because of this, it is not immediately apparent if siloxane compounds, for instance, will necessarily have a promoting effect due to their Si content alone, or whether their alternative structure will lead to other effects. Therefore, the evaluation of siloxanes impurities in syngas mixtures is an excellent opportunity for future work.

ACKNOWLEDGEMENTS

The authors acknowledge the generous support of the U.S. Department of Energy via the National Energy Technology Laboratory, Award Number DE-FE0007465 and the Department of Mechanical Engineering at the University of Michigan.

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Figure 1

Figure 2

Figure 3

Figure 4a

Figure 4b

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12a

Figure 12b

Figure 13