THE EFFECT OF IMPURITIES ON IGNITION DELAY TIMES AND LAMINAR FLAME SPEEDS OF SYNGAS MIXTURES AT GAS TURBINE CONDITIONS

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ABSTRACT

In addition to mostly H₂ and CO, syngas also contains reasonable amounts of light hydrocarbons, CO₂, H₂O, N₂, and Ar. Impurities such as NH₃, HCN, COS, H₂S, and NOx (NO, NO₂, N₂O) are also commonly found in syngas. The presence of these impurities, even in very low concentrations, can induce some large changes in combustion properties. Although they introduce potential design and operational issues for gas turbines, these changes in combustion properties due to the presence of impurities are still not well characterized. The aim of this work was therefore to investigate numerically the effect of the presence of impurities in realistic syngas compositions on some fundamental combustion properties of premixed systems such as laminar flame speed and ignition delay time, at realistic engine operating conditions. To perform this study, a state-of-the-art C0–C3 detailed kinetics mechanism was used. This mechanism was combined with recent, optimized sub-mechanisms for impurities which can impact the combustion properties of the syngas such as nitrogenous species (i.e., N₂O, NO₂, NH₄, and HCN) and sulfur-based species such as H₂S, SO₂ and COS. Several temperatures, pressures, and equivalence ratios were investigated. The results of this study showed that the addition of some impurities modifies notably the reactivity of the mixture. The ignition delay time is decreased by the addition of NO₂ and H₂S at the temperatures and pressures for which the HO₂ radical dominates the H₂ combustion. However, while NO₂ has no effect when OH is dominating, H₂S increases the ignition delay time in such conditions for pressures above 1 atm. The amplitude of these effects is however dependent on the impurity concentration. Laminar flame speeds are not sensitive to NO₂ addition but they are to NH₃ and HCN, inducing a small reduction of the laminar flame speed at fuel rich conditions. H₂S exhibits some inhibiting effects on the laminar flame speed but only for high concentrations. The inhibiting effects of NH₃, HCN, and H₂S are due to the OH radical consumption by these impurities, leading to the formation of radicals that are less reactive.

INTRODUCTION

Synthetic gas or syngas can be produced from nearly any type of carbonaceous feedstock. This wide array of possible sources in particular makes syngas an attractive fuel for dependable, clean, and efficient energy production using Integrated Gasification Combined Cycle (IGCC) plants or gas turbines. The syngas composition depends on the type of feedstock and on the process used to gasify it. The composition can include 6.8%–50.4% H₂, 8.1%–60.5% CO, 1.3%–29.6% CO₂, 0%–20.4% H₂O, 0%–9.3% CH₄ [1], and many impurities. Despite this complex composition, most of the studies on syngas have historically focused on H₂/CO only [2]–[26]. Few studies have also dealt with steam [8], CO₂ ([9],[11], [27]), N₂ [16], or realistic mixture compositions (although highly diluted in Ar for shock-tube data) [28],[29].

Recently, the effects of hydrocarbon addition (CH₄, C₂H₆, C₂H₄, and C₃H₆) were studied numerically at realistic gas turbine conditions for a series of syngas compositions (from the baseline CO/H₂ to real syngas mixture compositions) derived from biomass and coal feedstocks by the present authors [30]. The results of this study exhibited the great importance of hydrocarbons, even in small concentration, on fundamental combustion properties such as ignition delay time (τ_{ig}) and laminar flame speed (S_L). Indeed, while the CO/H₂ ratio was found to be of little importance due to the dominance of the hydrogen component, the addition of hydrocarbons increased τ_{ig}, notably under the conditions investigated. This increase was...
a function of the nature and concentration of the hydrocarbon and the pressure and temperature range. At 1 atm, \( \tau_{\text{ign}} \) was increased over the entire range of temperatures studied, whereas \( \tau_{\text{ign}} \) was increased only on the high-temperature side at 10 and 35 atm. This effect of the ignition delay time was mostly due to methane and ethylene. For the flame speed, however, ethane was found to be of larger importance, with a noticeable decrease in S. It was demonstrated in this previous study that the effects of the hydrocarbon addition are mostly due to reactions between the hydrocarbons and/or their radicals with the radical H, hence competing with the most important promoting reaction H + O\(_2\) ⇄ O + OH at the conditions of interest to gas turbine combustors.

The comparison between the baseline coal- and bio-derived syngases with averaged syngases (containing hydrocarbons, CO\(_2\), H\(_2\)O, N\(_2\)) showed a large difference in \( \tau_{\text{ign}} \) and in S. The impacts on the flame speed were due to both chemical and thermal (i.e. flame temperature) effects, whereas the effects on the ignition delay time were linked to the chemistry only. The main outcome of that recent study was that the baseline, binary CO/H\(_2\) mixtures generally studied are not in many cases good candidates to study syngas combustion under gas turbine conditions because they represent an over-simplified blend.

As mentioned earlier, in addition to these fuels and diluents, traces of impurities can also be found in syngas. These impurities are typically NH\(_3\), HCN, COS, H\(_2\)S, SO\(_2\), and NO\(_x\) (NO, NO\(_2\), N\(_2\)O), although some traces of HCl and metals have also been reported [5], [31]. While the concentration of these impurities is typically very low (up to 1.3% and 0.3% vol. for H\(_2\)S and HCN, respectively [32], 1.64% vol. for NH\(_3\) [33], 0.055 % vol. for SO\(_2\) and 0.123 % vol. for NO\(_x\) [34]), they can have a great impact on fuel combustion properties [35]. It is also worth mentioning that the combustion properties of syngas are, in most cases, driven by hydrogen combustion chemistry [1], [26]-[30]. Recent studies with H\(_2\) mixtures seeded with small amounts of NO\(_2\) [36] and H\(_2\)S [38] exhibited a great influence of these impurities on \( \tau_{\text{ign}} \) (generally promoting for NO\(_2\) and generally inhibiting for H\(_2\)S). However, except for NH\(_3\) [29], there is no study on the influence of these impurities on realistic syngas combustion. There is also no study on the potential interactions between these impurities during syngas combustion.

Since kinetics models for these impurities have been recently optimized (Mathieu et al. for NO\(_2\) [36], N\(_2\)O [37], H\(_2\)S [38], NH\(_2\)/H\(_2\)/NO\(_x\) [39], Glarborg et al. for HCN [40], COS [41]), it is now possible to investigate numerically, with a reasonable degree of accuracy, the effects of these impurities on syngas combustion properties. The aim of the present study was therefore to perform such a numerical investigation for fundamental combustion properties of premixed systems, i.e., laminar flame speed and ignition delay time. Realistic engine operating conditions were selected, and various syngas compositions were studied.

The syngas compositions defined in Mathieu et al. [30] were used to define neat baselines for bio- and coal-derived syngases herein. These baseline mixtures were then computationally seeded with various impurities specific to each type of syngas to exhibit their effects on combustion properties of interest herein. All of the mixtures investigated and the modeling procedure details are covered first in this paper. The results of the calculations are then presented and discussed, with emphasis on the significant chemical kinetics reactions.

**MODELING PROCEDURE**

The detailed chemical kinetics model used herein is based on the C0-C3 mechanism, AramcoMech 1.3, developed at the National University of Ireland, Galway (NUIG) [42]. A high-temperature version of this model, where low-temperature species (peroxy radicals, alkyl hydroperoxides, keto-hydroperoxides, etc.) and reactions were removed, was used for flame speed calculations. To this base mechanism were added the sub-mechanisms for H\(_2\)/H\(_2\)S [38] and NH\(_2\)/H\(_2\)/NO\(_x\) [39]. The HCN mechanism was added to the NH\(_3\) part and has been unchanged from the work of Glarborg et al. [40]. The COS sub-mechanism is from a recent paper from Glarborg et al. [41], while the NO\(_x\)-HC interactions were taken from the work of Sivaramakrishnan et al. [43]. The complete mechanism comprises 1,331 reactions and 198 species, while the high-temperature mechanism consists of 188 species and 1,243 reactions. The modeling of the various syngas mixtures was done with air as the oxidant. The Chemkin package 10112 was used to perform the numerical calculations. Ignition delay time calculations were performed using the Closed Homogeneous Batch Reactor model with the Constant Volume assumption, while the Premixed Laminar Flame Speed Calculation model was used to compute the laminar flame speeds.

**MIXTURES INVESTIGATED**

The two first mixtures studied were the baseline (CO/H\(_2\)) coal- and bio-derived syngas mixtures in air (60/40 and 50/50 (mol.), respectively). These neat mixtures were then seeded with single impurities (COS, NH\(_3\), and H\(_2\)S for the coal syngas and NO\(_2\), NH\(_3\), HCN, and SO\(_2\) for the bio-syngas) at their maximum reported concentration [32]–[34] to estimate the effect of impurities on \( \tau_{\text{ign}} \) and S on these baseline mixtures. Note that due to their possible large concentration and presumably great effects on combustion properties, NO\(_2\) and H\(_2\)S have also been studied at averaged concentrations that have been determined from several syngas mixture compositions ([2]–[5], [32]–[34]). For each type of syngas, a mixture containing all the aforementioned impurities at their maximum reported concentration was also investigated, to exhibit possible synergistic or antagonistic effects between impurities.

In addition to these baseline syngases, averaged, realistic, mixtures, containing H\(_2\)/CO, H\(_2\)O, N\(_2\), CO\(_2\), and small hydrocarbons (but without other impurities) were also defined. More details on these realistic mixtures and on the effects of hydrocarbons on \( \tau_{\text{ign}} \) and S are available in Mathieu et al. [30]. Effects of NO\(_2\) and H\(_2\)S at averaged and maximum reported concentrations for, respectively, these realistic bio- and coal-
derived syngases were investigated. Finally, the realistic syngases were also studied with the maximum reported concentration of all impurities specific to each type of syngas. The compositions of the mixtures investigated in this study are provided in Tables 1 and 2 for the bio- and coal derived syngas, the concentration of all impurities specific to each type of syngas.

Flame speed computations were performed at 1 and 15 atm; between $\phi = 0.5$ and 3.0; and for unburned gas temperatures ($T_u$) of 300 and 500 K. These conditions were selected since the model has been validated against data obtained for this range of temperatures (see Metcalfe et al. [42] and references therein). Nevertheless, some calculations were also performed at a more realistic post-compression temperature of 700 K. Ignition delay time computations were performed between 900 and 1400 K; at 1, 10, and 35 atm; and for an equivalence ratio of $\phi = 0.5$. Note that the temperature range for $\tau_{ign}$ calculations is well above the inlet temperature range encountered in most of the gas turbines. This range of temperature was however selected since the Alstom SEV, used as a reference in this study, presents an inlet temperature higher than 1000 K. Stoichiometric mixtures were also investigated for the neat mixtures as well as for the mixtures with all the impurities. The ignition delay time was defined by the step rise in the OH* signal, which occurs at ignition, as visible in Fig. 1. As can be seen, a similar result would have been obtained using the pressure signal, even though a slow and very moderate pressure increase can be observed before the ignition.

MODEL VALIDATION

While the base C0–C3 mechanism has been validated against a large body of hydrogen and syngas data from the literature (see [26], [30] and [42]), it is however worth mentioning that there are very few experimental results available for syngas mixtures with impurities. To the best of the authors’ knowledge, the only results available are the results from Mathieu et al. [29] where ignition delay times for baseline (H$_2$ and CO only) and realistic (H$_2$, CO, CO$_2$, CH$_4$, and H$_2$O) bio-syngas mixtures diluted in Ar, with and without NH$_3$, were measured at various pressures. These results were computed with the detailed kinetics mechanism described above, and the results are visible in Fig. 2 for the baseline mixture and in Fig. 3 for the realistic mixture. As can be seen in Fig. 2, the model captures very well the experimental trends for all pressure conditions. Data at 30 atm were perfectly reproduced, and the lack of effect of NH$_3$ is captured. At 10 atm, $\tau_{ign}$ are also perfectly reproduced by the model, except for the highest temperature when NH$_3$ is in the mixture, where a small discrepancy can be observed. While the model predicts a very small increase in $\tau_{ign}$ at this pressure when ammonia is added, it is difficult to observe such a small increase from the experimental results. At the lowest pressure investigated, the results are generally well reproduced except for the lowest temperatures where the model is under-reactive. The very small decrease in the ignition delay time observed when NH$_3$ is added, over most of the temperature range, can be observed both in the experiments and in the modeling at this pressure condition.

Fig. 1: Determination method for the ignition delay time using the computed pressure and OH* mole fraction profiles.

For the realistic biosyngas mixture, Fig. 3, the experimental trends associated with the pressure condition and the presence of NH$_3$ (very small increase in the ignition delay time for the latter case) are also captured by the model. However, for this type of mixture, the model tends to be under-reactive, especially on the low-temperatures side at 1.7 atm (by a factor 1.8) and on the high-temperatures side for higher pressures (by factors of 1.7 and 3.5 at 10 and 35 atm, respectively).

This validation stage shows the ability of the model to reproduce experimental trends with good accuracy in the results. This comparison demonstrates the relevance of the mechanism used in this study to conduct a numerical investigation for the temperature and pressure range relevant to gas turbines.

RESULTS

The results are presented as follows: first, the calculations for the neat baseline mixtures (CO and H$_2$ only) are covered to study the effect of the H$_2$/CO ratio. This series is followed by the effect of the impurity additions on these baseline mixtures. Finally, the averaged syngas mixtures including all species are considered with and without impurities. As it is shown below, one of the outcomes of this study is that trends on the effects of impurity additions observed for the baseline bio- or coal-syngas are the same as for the averaged syngases. To avoid redundancy, only the results for the biosyngas are presented in the baseline syngas section, whereas results for the averaged coal syngas are presented in the averaged mixtures section. The results obtained with the other type of syngas are briefly described, and the comparison between the two types of syngas is visible in each section.
this study at various pressure conditions.

Fig. 2: Comparison between ignition delay times for a biosyngas mixture diluted in Ar, with and without NH3, from Mathieu et al. [29] and the model used in this study at various pressure conditions.

The figures for the baseline coal-syngas and averaged bio-syngas are visible in the Annex Section. For each general category, the ignition delay time results are discussed first, followed by the laminar flame speed results.

Table 1 Bio-syngas mixtures investigated (mole fraction).

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<th>Mixture</th>
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Table 2 Coal-syngas mixtures investigated (mole fraction).

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<th>Mixture</th>
<th>H2</th>
<th>CO</th>
<th>CH4</th>
<th>C2H6</th>
<th>C2H4</th>
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<th>H2O</th>
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<th>NH3</th>
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Baseline Bio-syngas

0.005 H2 / 0.005 CO / 0.01 O2 / 0.98Ar

1.7 atm neat
1.7 atm + 200 ppm NH3
12.1 atm neat
12.7 atm + 200 ppm NH3
32.1 atm neat
31.7 atm + 200 ppm NH3

Model - neat
Model - NH3

Fig. 2: Comparison between ignition delay times for a baseline (H2/CO) biosyngas mixture diluted in Ar, with and without NH3, from Mathieu et al. [29] and the model used in this study at various pressure conditions.

Baseline Mixtures

Ignition Delay Time

The effects of the ratio between CO and H2 on the ignition delay time, for the three pressure conditions investigated, are typically small, as can be seen in Mathieu et al. [30]. Therefore, the small change in the CO/H2 ratio between the coal- and biosyngases investigated herein does not really alter the predicted ignition delay times for these neat baseline mixtures, regardless of the temperature or pressure.

One can mention that the main difference between these two syngases is that the ignition delay times are slightly shorter for the mixture that contains the higher proportion of H2 (biosyngas), but no change in the behavior was reported. One can also mention the important, and temperature-dependent, effect of pressure on the ignition delay time (see Mathieu et al. [30]).
various pressure conditions. Mathieu et al. [29] and the model used in this study at intermediate-temperature range. This reason explains why low-pressure experiments show a stronger reactivity than high-pressure experiments at the reactivity. This pressure dependence is due to the increased collisional efficiency of \( r_2 \) which decreases the overall reaction. In addition, the transition from \( r_2 \) to \( r_1 \) is shifted to higher temperatures when the pressure is increased. This pressure dependence is due to the increased collisional efficiency of \( r_2 \) which decreases the overall reaction. This reason explains why low-pressure experiments show a stronger reactivity than high-pressure experiments at the intermediate-temperature range.

Laminar Flame Speed

Although the laminar flame speed for syngas mixtures was investigated for several temperatures and pressures, only two examples with the extreme conditions are discussed here. The trends and conclusions drawn from these two examples are indeed the same for the two other conditions, not shown. The difference between the neat baseline mixtures was discussed in detail previously [30]. The two figures are therefore visible in the Annex Section of this paper (Figs. A1 and A2). At 1 atm for an inlet temperature of 300 K, the difference between the two types of syngas can be relatively important for this combustion property; the blend with the lowest amount of \( H_2 \) has the lowest flame speed, especially at fuel rich conditions. The difference between the two mixtures is close to 30 cm/s. Similar observations can be made for the 15-atm, 500-K condition, the difference being a little larger (45 cm/s). Note that the largest difference between the two syngases was observed for the 1-atm, 500-K case, which also corresponds to the condition where the flame speeds are the highest.

Impurity Addition to the Baseline Mixtures

Ignition Delay Time

The effects of impurity addition on the baseline bio-syngas mixture are visible in Figs. 4 (1 atm), 5 (10 atm), and 6 (35 atm). As can be seen in Fig. 4, only NO\(_2\) seems to have an effect (promoting) on the ignition delay time, for temperatures lower than 1000 K. The differences in \( \tau_{\text{ign}} \) induced by NH\(_3\), HCN, or SO\(_2\) are indeed too small to be discernible. At 900 K, the ignition delay time is reduced by about 85% by the addition of 400 ppm of NO\(_2\), and this reduction in \( \tau_{\text{ign}} \) reaches 92% for the highest NO\(_2\) concentration investigated (bBiosyn-NO\(_2\)-Hi mixture). The ignition delay times for the mixture containing all the impurities at their highest level are nearly the same as for the bBiosyn-NO\(_2\)-Hi mixture, which indicates that there is no important interaction between the impurities at this condition.

Fig. 3: Comparison between ignition delay times for a bio-syngas mixture diluted in Ar, with and without NH\(_3\), from Mathieu et al. [29] and the model used in this study at various pressure conditions.

These effects were discussed in detail already [26], [30] and are essentially due to the competition between two reactions: the chain-branching reaction \( H + O_2 \rightleftharpoons O + OH \) (r1) and the chain-propagating reaction \( H + O_2 (\pm M) \rightleftharpoons HO_2 (\pm M) \) (r2). While r1 controls the reactivity at higher temperature, r2 is dominant at lower temperature. In addition, the transition from r2 to r1 is shifted to higher temperatures when the pressure is increased. This pressure dependence is due to the increased collisional efficiency of r2 which decreases the overall reactivity. This reason explains why low-pressure experiments show a stronger reactivity than high-pressure experiments at the intermediate-temperature range.

Fig. 4: Effect of various impurities on the ignition delay time for a baseline bio-syngas mixture at 1 atm.

At 10 atm (Fig. 5), similarly, only NO\(_2\) has an effect on \( \tau_{\text{ign}} \). This effect starts at higher temperatures, below 1150 K, and is less important than for the previous case: 23% and 45% reduction at 900 K for the bBiosyn-NO\(_2\)-Av and bBiosyn-NO\(_2\)-Hi mixtures, respectively. A similar trend is followed at higher pressure, Fig. 6, where NO\(_2\) has some effect at temperatures below 1250 K but with reductions in \( \tau_{\text{ign}} \) that are less important: \( \tau_{\text{ign}} \) are around 19% shorter with an addition of 400 ppm of NO\(_2\) and by around 36% with 1200 ppm of NO\(_2\) at 900 K.

The effects on \( \tau_{\text{ign}} \) of impurities that are more specific to coal syngas also showed that an addition of NH\(_3\) does not modify the ignition delay time over the range of conditions investigated. A similar absence of any effect was observed with COS. However, if an averaged concentration of H\(_2\)S did not have a distinguishable effect on \( \tau_{\text{ign}} \), a relatively large concentration of this contaminant exhibited a large effect on the ignition delay time, as it is shown later with the averaged coal-syngas mixture section, for which trends are the same.
It is also worth noting here that the mixture with all the impurities yields the same results as the coal-syngas mixture with the highest concentration of H$_2$S, indicating that there is no interaction between impurities at these conditions.

The effect of the equivalence ratio was also investigated in this study. Since this effect has been studied already by the authors [30] with neat mixtures, corresponding figures for the three pressure conditions investigated are visible in the Annex Section of this paper (Fig. A4 for bBiosyn and Fig. A5 for bCoalsyn). To summarize these results, increasing $\phi$ from 0.5 to 1.0 has nearly no effect on $\tau_{\text{ign}}$ at 1 atm for the bBiosyn mixture. A small decrease in the reactivity is observed at the two temperature extremities at 10 atm (4.5% difference at the highest temperature and up to 13.7% for the lowest temperature), while the decrease in the reactivity covered most of the temperature range at 35 atm. Similar results were observed for the bCoalsyn mixture.

In the presence of impurities, Fig. 7, the ignition delay times of a baseline bio-syngas mixture doped with impurities seem to be modified in larger proportion by a change in the equivalence ratio than for the neat mixture. The ignition delay time is indeed decreased by between 20% (1400 K) and 45% (900 K) at 1 atm and up to 55% at 10 atm, 900 K. For the highest pressure investigated, the reduction in $\tau_{\text{ign}}$ is between 25% at 1400 K and 50% at 900 K.

Concerning the baseline coal-syngas mixture with impurities, Fig. 8, the effect of the equivalence ratio on $\tau_{\text{ign}}$ seems a bit more complex. The ignition delay time is slightly increased at 1 atm for temperatures above 950 K and is decreased below this temperature. It is also worth mentioning that similar behavior is observed at 10 atm, with the pivot temperature being around 1135 K. At 35 atm, $\tau_{\text{ign}}$ are shorter for the highest equivalence ratio over the entire range of temperature investigated, the decrease being very small at high temperature and above 35% at 900 K.

It is interesting to compare the effects of hydrocarbon addition, investigated in Mathieu et al. [30], with the effects of impurity addition on the baseline syngas mixtures investigated herein. As can be seen in Fig. 9 for the bBiosyn mixture, the effects from hydrocarbon addition are overall higher than the effects for impurity addition. This is particularly true at 1 atm where a large effect of hydrocarbon addition is visible over the entire range of conditions for the low-temperature side only for the impurities. At 10 atm, it is interesting to see that the effects of hydrocarbons are visible only on the high-temperature side, whereas the impurity effect is still observed for low temperatures at this pressure condition. The same behavior is observed for the 35-atm case, although the effects of both hydrocarbons and impurities are smaller at this pressure condition. Similar observations can be made for the coal-syngas mixture, although the hydrocarbon-addition effects are less important in this case (not shown).
Laminar Flame Speed

The effects on the laminar flame speed of various impurities with \( \text{bBiosyn} \) at 1 atm, 300 K and 15 atm, 500 K as initial conditions are visible in Fig. 10 and Fig. 11, respectively. As can be seen in Fig. 10, the addition of impurities has a small effect on the laminar flame speed and this effect is visible for fuel rich conditions only, for an equivalence ratio larger than 1.5. Results are also somewhat contrary to what has been observed for the ignition delay time: the reactivity of the mixture is decreased by the impurity addition, and this effect is found for all the impurities except \( \text{NO}_2 \) and \( \text{SO}_2 \). The largest effect is provided by \( \text{NH}_3 \) (reduction of the maximum \( S_L \) by 5 cm/s), and the maximum laminar flame speed is only reduced by a few cm/s, from 191 to 189 cm/s, for the 0.28% \( \text{NH}_3 \) addition. When all the impurities are added together, the laminar flame speed is further reduced. However, the reduction corresponds to the sum of the effects from \( \text{NH}_3 \) and HCN, indicating that there is no enhancing or inhibiting interaction between these impurities.

At the other extreme condition, 500 K and 15 atm (Fig. 11), laminar flame speeds are higher but trends in the results are similar. However, the decrease in the laminar flame speed with impurities is slightly larger, for example from 271 to 258 cm/s with \( \text{NH}_3 \).

For the \( \text{bCoalsyn} \) mixture, a decrease in the laminar flame speed was observed with the \( \text{NH}_3 \) addition and with the highest \( \text{H}_2\text{S} \) concentration. As for the \( \text{bBiosyn} \) mixtures, these effects are observed for \( \phi > 1.5 \) only and the effects of impurities on \( S_L \) seem to add to each other without apparent interaction.

The influence of impurity addition on the baseline biosyngas can be compared to the effects of hydrocarbon...
addition at 15 atm and 500 K in Fig. 12. It is visible in this figure that the effect of impurities is significantly smaller than the effect of hydrocarbons. As seen, a 66% decrease in $S_L$ was observed for the hydrocarbon addition (with a maximum in $S_L$ observed at $\phi = 2.0$ for the baseline and 1.2 for the hydrocarbon addition) and around 6% for the impurities. The same tendency was observed for the other conditions investigated (not shown). The same comparison between the effects of impurities and hydrocarbons was made for the baseline coal syngas at 500 K, 15 atm (Fig. 13).

First, one can notice from Figs. 12 and 13 that the effects of impurities are more important (while the effects of the hydrocarbons are smaller) for the coal syngas than for the bio-syngas. As a result, while a significant difference can be observed between these two kinds of additions, the difference is not as large as for the bio-syngas ($S_L$ reduction of 13% by impurities and 51% by hydrocarbons).

**Impurity Addition to the Average Mixtures**

**Ignition Delay Time**

A comparison between the ignition delay times of the two averaged mixtures (from coal and biomass) for the three pressure conditions investigated has been made in Mathieu et al. [30]. Some significant differences between these two mixtures were observed due to the difference in hydrocarbon composition. The figure comparing these two mixtures is visible in the Annex Section (Fig. A5). The equivalence ratio effect for the two average mixtures is visible in the authors' previous work [30]. The effects of impurities on the Coalsyn mixture at 1 atm are visible in Fig 14. As can be seen, the average concentration of $\text{H}_2\text{S}$ has no effect on $\tau_{\text{ign}}$ at this condition.

The ignition delay time is however notably increased for temperatures above 975 K by a factor between 2 (1400 K) and 5 (1050 K) for the highest $\text{H}_2\text{S}$ concentration. The calculations yield the same result for the Coalsyn-impur mixture, indicating that the other impurities have no effect overall.

At 10 (Fig. 15) and 35 atm (Fig. 16), the results obtained with the lowest concentration of $\text{H}_2\text{S}$ investigated are without effect. However, a noticeable effect on the ignition delay time is exhibited by the high $\text{H}_2\text{S}$ concentration and, again, no further effect is seen with all impurities. At 10 atm, the $\text{H}_2\text{S}$ addition decreases $\tau_{\text{ign}}$ below 1225 K and increases it above this temperature. At 35 atm, ignition delay times are not changed by the impurity addition at 1400 K.

However, below this temperature, a noticeable decrease can be observed with the highest $\text{H}_2\text{S}$ concentration, this decrease being larger as the temperature decreases. For the average bio-syngas mixture, as for the baseline mixtures, only
NO\textsubscript{2} has an effect on $\tau_{\text{ign}}$. Ignition delay times are notably decreased below 1000 K in the presence of NO\textsubscript{2}; the amplitude of this decrease being proportional to the concentration of NO\textsubscript{2} at the authors’ conditions. The ignition delay times for the mixture with all the impurities are similar to the ones from the high NO\textsubscript{2} concentration mixture, indicating a lack of effect between NH\textsubscript{3}, HCN, and SO\textsubscript{2}. Results for the averaged bio-syngas are visible in the Annex section of the paper (Figs. A12-A14).

At higher pressure, Fig. 18, $S_L$ are significantly smaller, with a reduction higher than 50% due to the initial pressure increase. Impurity effects are the same as for the low-pressure case, and the percentage reduction in the maximum laminar flame speed is also the same as for the previous case with lower initial pressure. A higher temperature (700 K) more representative of conditions encountered in gas turbine was also investigated in Fig. 18. As can be seen, the trends are the same as for 500 K--the reduction in $S_L$ due to the impurities being still around 9%. This scalability of the results to higher temperatures shows that the conditions investigated in this study and the conclusions drawn from these results are also valid for gas turbine conditions with more realistic (i.e., higher) inlet temperatures.

**DISCUSSION**

For the bio-syngas mixtures, the results showed that NO\textsubscript{2} was the only impurity to have an effect on $\tau_{\text{ign}}$. This effect is present only when the low-temperature chemistry of H\textsubscript{2} rules the combustion (i.e. when the HO\textsubscript{2} radical dominates over OH). This behavior indicates a purely chemical mechanism due to the reaction NO + HO\textsubscript{2} $\rightleftharpoons$ NO\textsubscript{2} + OH (r3) (NO\textsubscript{2} being mostly converted to NO by the reaction NO\textsubscript{2} + H $\rightleftharpoons$ NO + OH (r4)). The OH radicals produced then oxidize the hydrogen via OH + H\textsubscript{2} $\rightleftharpoons$ H\textsubscript{2}O + H (r5), and this reaction then allows recycling NO via r4. This catalytic effect of NO\textsubscript{2} which transforms HO\textsubscript{2} into OH explains the large effects observed on the ignition delay time, when the low-temperature chemistry was dominant.
The lack of effect of NO₂ on the flame speed, where the high-temperature chemistry of H₂ dominates, associated with the unmodified flame temperature, confirms the chemical role of NO₂. For the typical coal baseline syngas, H₂S is the only contaminant that has an influence on the ignition delay time. An effect on the laminar flame speed was observed too, with the highest impurity concentration studied. The inhibiting effect occurring at high temperature for ignition or with the laminar flame speed is due to the reaction H₂S + H ⇄ SH + H₂ (r6) which occurs before the ignition and inhibits the dominating reaction H + O₂ ⇄ OH + O (r1) and reduces the overall reactivity of the mixture. The H₂S can therefore be viewed as a sink for H radicals, preventing r1 to take place and to trigger the ignition. The absence of change in the flame temperature, even for the highest H₂S concentration investigated, indicates a purely chemical effect of H₂S on the laminar flame speed. At this condition, the high-temperature mechanism via r6 is responsible for the decrease in the mixture’s reactivity. For the conditions where H₂S is promoting the reactivity of the ignition delay time, this result can be explained by the fact that H₂S reacts with radicals (H, O, OH, and HO₂) to give SH + products, and this radical consumption limits the important reactions for H₂ oxidation, namely H + O₂ ⇄ O + OH (r1) and H + O₂ +M ⇄ HO₂ + M (r2), the latter being more important at these conditions. Most of the SH will then either quickly form SO which will then form SO₂ via the reaction SO + O₂ ⇄ SO₂ + O or react through SH + SH ⇄ H₂S + S (r7). The S produced will then react through S + O₂ ⇄ SO + O (r8) and SO + O₂ ⇄ SO₂ + O (r9).

To summarize, at conditions where r2 dominates, the formation of HO₂ is limited by the presence of H₂S via the consumption of H radicals (r6) whereas the SH produced will then lead to the formation of O radicals via r8 and r9. These O radicals will then react through O + H₂ ⇄ OH + H (r10) and, overall, promote the reactivity of the mixture compared to the conditions where r2 was dominant, without H₂S.

Although NH₃ and HCN addition did not exhibit any effect on the ignition delay time, these components reduced the flame speeds for the baseline mixtures, mostly on the fuel rich side. These inhibiting effects are purely chemical effects as the adiabatic flame temperature is nearly unchanged by the presence of these components. This result is visible for the NH₃ case in Fig. 19, where all the adiabatic flame temperatures are the same for a given equivalence ratio, regardless of the nature or concentration of the contaminants.

CONCLUSIONS

In this paper, the effects of impurities on fundamental combustion properties of premixed systems fueled with bio- or coal-derived syngases were investigated over a wide range of conditions relevant to gas turbine combustion. The results of this study show that not all the impurities have an effect on the ignition delay time or laminar flame speed. The concentration of the impurities, the temperature, and the pressure are also important factors governing the influence of impurities. While the effects of impurities are typically less important than for hydrocarbons, these effects appear to be linked to the chemistry only, as no noticeable flame temperature change was observed.

Fig. 18: Effect of various impurities on the laminar flame speed for an average coal-syngas mixture at 15 atm, 500 K and 700 K as initial conditions.

Fig. 19: Effect of various impurities on the adiabatic flame temperature for an average bio-syngas mixture at 15 atm, 500K as initial conditions.
NO₂ showed some promoting effects on the ignition delay time at conditions where the HO₂ radical was dominant. For the high-temperature flame speed process, HO₂ radicals do not play an important role, explaining the lack of effect of NO₂ on the Sₐ. When H₂S, NH₃, and HCN are in the mixture, they will tend to react with H radicals and to produce radicals that present a lower reactivity than OH, hence reducing the reactivity of the mixture by limiting r1 (H + O₂ ⇄ O + OH). However, H₂S will also have a promoting effect on the ignition delay time for conditions where the HO₂ radical is important (low-temperature, high-pressure conditions for the ignition delay time predictions). This lower-temperature behavior is due to a decrease in the r2 pathway (H + O₂ + M ⇄ HO₂ + M) due to the reaction r6 (H₂S + H ⇄ SH + H₂) followed by enhancing reactions (compared to r2) that will lead to r10 (O + H₂ ⇄ OH + H). COS and SO₂ are the only impurities that do not exhibit any effect on both the syngas laminar flame speed and the ignition delay time under the conditions investigated. One can conclude that these two species can be neglected when considering the combustion properties of realistic syngas mixtures at gas turbine conditions.

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REFERENCES


ANNEX A

ADDITIONAL RESULTS

Fig. A1 Laminar flame speeds for baseline bio- and coal syngas mixtures (CO/ H₂ and 60 CO / 40 H₂, respectively) with 1 atm and 300 K as initial conditions.

Fig. A2 Laminar flame speeds for baseline bio- and coal syngas mixtures (CO/ H₂ and 60 CO / 40 H₂, respectively) with 15 atm and 500 K as initial conditions.

Fig. A3 Equivalence ratio effect on the ignition delay time for a baseline bio-syngas mixture at 1, 10, and 35 atm.

Fig. A4 Equivalence ratio effect on the ignition delay time for a baseline coal-syngas mixture at 1, 10, and 35 atm.
Fig. A5: Comparison between the ignition delay time of averaged bio-syngas and coal-syngas mixtures at $\phi = 0.5$ and at 1, 10, and 35 atm.

Fig. A9: Impurity- and hydrocarbon-addition effects on the ignition delay time of a baseline coal-syngas mixture at $\phi = 0.5$ and at 1, 10, and 35 atm.

Fig. A10: Laminar flame speeds for a baseline coal syngas with various impurities at 1 atm and 300 K as initial conditions.

Fig. A11: Laminar flame speeds for a baseline coal syngas with various impurities and at 15 atm and 500 K as initial conditions.
Fig. A12: Effect of various impurities on the ignition delay time for an average bio-syngas mixture at 1 atm.

Fig. A13: Effect of various impurities on the ignition delay time for an average bio-syngas mixture at 10 atm.

Fig. A14: Effect of various impurities on the ignition delay time for an average bio-syngas mixture at 35 atm.