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# Analytical prediction of syngas induction times

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ABSTRACT

Computations indicate that, under all possible conditions of practical interest, including temperatures both above and below the crossover temperature at which the rates of the $H_2 + O_2$ branching and termination steps are equal, twelve irreversible elementary steps suffice to provide accurate values of induction times in autoignition processes of fuels consisting of mixtures of $H_2$, CO, and inerts. At high temperatures, this time is controlled by the time required for the radical pool to reach a steady state, with heat release being negligible during that time. This time is approximated well by the time that it would take for $HO_2$ to reach a steady state if its consumption rate were dominated by formation of $H_2O_2$ at all temperatures, as it is at low temperatures. Below the crossover temperature, the time to reach an $HO_2$ steady state becomes shorter than the induction time, and the heat release becomes non-negligible once $HO_2$ has reached a steady state, resulting in the induction time progressively approaching that of a thermal explosion, which includes an effectively autocatalytic production of $H_2O_2$. On the basis of these observations, analytical approximations are introduced here that enable induction times to be calculated accurately under all conditions.



## 1. Introduction

There is increasing interest in the use of fuels produced synthetically, for example by gasification of coal or of biomass, in combustion systems such as gas turbines [1] and internal combustion engines [2]. These syngas fuels usually are predominantly mixtures of hydrogen, carbon monoxide, and inert constituents, although they often contain appreciable amounts of methane and other hydrocarbons [3]. Even when these additional species are present, however, the combustion characteristics of the syngas often can be described reasonably well by the combustion chemistry of mixtures of $H_2$ and CO. A number of detailed chemical-kinetic mechanisms for the combustion of such mixtures are available in the literature [4–8]. These mechanisms, which may still have inaccuracies at high pressures and low temperatures but nevertheless produce reasonable agreements with measurements in most respects, typically involve on the order of fifty or more elementary steps, which is large enough to cause them to be expensive or impossible to employ in certain applications involving computational fluid dynamics (CFD). It is therefore worthwhile to investigate the development of simpler approaches for solving specific related problems.

One problem, of special importance in gas-turbine applications, for example, is the autoignition problem. There is, in particular, considerable interest in ignition-delay times, or so-called induction times, in connection with flashback concerns for gas turbines operating on syngas. The combustion in properly operating gas turbines must be confined to the combustion chamber, but, especially when the fuel is syngas of high hydrogen content, autoignition may occur upstream, causing the combustion to flash back into the feed stream, sometimes with catastrophic results [9]. This phenomenon arises when the induction time is shorter than the residence time of the gas mixtures in the feed streams. Under idealized condition, the induction time can be defined as the time required for a uniform fuel-oxidizer gas mixture, placed at time zero in an isobaric or isochoric, adiabatic chamber, to begin to release heat rapidly. Such an idealized definition remains ambiguous until a specific definition is given for the phrase “begin to release heat rapidly”. There are many different possible definitions for this phrase, all of which correspond to different values of the induction time, but under a wide range of conditions of practical interest, once a small amount of heat release occurs, the rate of heat release accelerates very rapidly, so that the different definitions produce induction-time values that differ very little. The present contribution employs the time of maximum rate of heat release as the ignition-time definition, but the result was found to be the same as the time required for the temperature to increase by 200 K or achieving a rate of temperature rise greater than 10,000 K/s.

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In real-world scenarios, such as those that occur during the gas-turbine flashback mentioned above, mixture compositions and temperatures vary in space and time, so that a single idealized induction time is not directly relevant. The complete, detailed, chemical-kinetic mechanisms, however, are not needed if interest resides solely in the autoignition problem in these cases. The elementary chemistry that successfully describes the idealized induction times over the complete range of conditions experienced by the gas in the practical situation also can correctly predict the autoignition in the application, through appropriate CFD, when the spatial and temporal variations are taken into account. It therefore is worthwhile to identify simplified chemistry with fewer elementary reactions that is successful in wide-range induction-time predictions. This has been done in the present work. The following section presents a short chemical-kinetic mechanism, consisting of only twelve irreversible elementary steps, which predicts induction times that agree over all conditions considered with those obtained with a 30-step detailed mechanism. The reaction rates of the short mechanism involve the concentrations of $H_2$, CO, $O_2$, H, O, OH, $HO_2$, and $H_2O_2$, but are practically independent of the concentrations of $CO_2$ and $H_2O$, which appear only indirectly through the chaperon efficiencies of the three-body recombination reactions. Since consumption of reactants $H_2$, CO, and $O_2$ and production of products $CO_2$ and $H_2O$ are small during ignition, the number of reacting-species equations that need to be considered is reduced from 10 to 5, and, together with the decrease in the number of elementary steps, this has been found in our representative computational investigations to result in a reduction of the associated computational time by about 30%, thereby facilitating many types of numerical investigations. It should be cautioned that this chemistry will not correctly predict the subsequent combustion, but it will be reliable for autoignition events, affording utility in associated design and diagnostic tasks.

It is also of interest to have explicit analytical formulas for the idealized induction times. Such formulas are helpful, for example, in making preliminary estimates of autoignition processes, prior to CFD investigations. Such formulas have often been derived before under restricted conditions [10–12]. In general, however, those restricted conditions cannot be guaranteed to be encountered in applications, and therefore formulas with wider ranges of validity are desired. By use of our simplified chemistry, such wide-range induction-time formulas are derived here for isobaric, adiabatic conditions. This entails identifying both the controlling autoignition processes over the full range of conditions and corresponding useful specific definitions of induction times. Those developments are presented in subsequent sections of the paper.

The results for the homogeneous ignition problem addressed here can be useful in understanding more complex scenarios, including the nonuniform time-varying environments found in reciprocating engines, where conditions evolve from the low-temperature to the high-temperature regimes identified below, necessarily complicating the required analysis. Although the results presented specifically pertain to mixtures of CO–$H_2$ with air, all of the conclusions, as well as the analytic formulae derived, apply also to ignition employing pure $O_2$ or general $O_2$-inert oxidizer mixtures with various degrees of dilution.

## 2. Simplified chemistry for syngas ignition

Table 1 lists the elementary steps with their associated rate parameters for a 12-step mechanism that describes syngas chemistry during ignition as accurately as any detailed mechanism. The values of the rate parameters in the table are taken from the San Diego mechanism [13], which includes recently updated rate information for the first eight steps [14]. Figure 1 compares predictions of induction times by this mechanism with predictions obtained with the corresponding full detailed mechanism for a range of conditions, including those for which the predictions from Table 1 are the worst. It is seen from this figure that the differences are almost completely indistinguishable in all cases. This mechanism has been selected specifically to address ignition delay times, and other steps, as well as reverse reactions, become important in addressing other questions, especially at high temperatures. For the two mixtures in Fig. 1, at the same pressure and initial temperature, the ignition delays differ by a factor of order unity, an aspect of the problem to be further addressed in Fig. 9.

**Table 1**
Rate coefficients responsible for syngas ignition in Arrhenius form $k = AT^n \exp(-E/R^oT)$ for the skeletal mechanism, with numerical values of the San Diego mechanism [13].

| | Reaction | | $A$[a] | $n$[a] | $E$[a] |
|---|---|---|---|---|---|
| 1 | $H+O_2 \rightarrow OH+O$ | | $3.52\ 10^{16}$ | −0.7 | 71.42 |
| 2 | $H_2+O \rightarrow OH+H$ | | $5.06\ 10^{4}$ | 2.67 | 26.32 |
| 3 | $H_2+OH \rightarrow H_2O+H$ | | $1.17\ 10^{9}$ | 1.3 | 15.17 |
| 4 | $H+O_2+M \rightarrow HO_2+M$[b] | $k_0$ | $5.75\ 10^{19}$ | −1.4 | 0.0 |
| | | $k_\infty$ | $4.65\ 10^{12}$ | 0.44 | 0.0 |
| 5 | $H_2+O_2 \rightarrow HO_2+H$ | | $2.93\ 10^{12}$ | 0.356 | 232.21 |
| 6[c] | $2HO_2 \rightarrow H_2O_2+O_2$ | | $1.03\ 10^{14}$ | 0.0 | 46.22 |
| | | | $1.94\ 10^{11}$ | 0.0 | −5,89 |
| 7 | $HO_2+H_2 \rightarrow H_2O_2+H$ | | $7.80\ 10^{10}$ | 0.61 | 100.14 |
| 8 | $H_2O_2+M \rightarrow 2OH+M$[d] | $k_0$ | $7.60\ 10^{30}$ | −4.20 | 213.71 |
| | | $k_\infty$ | $2.63\ 10^{19}$ | −1.27 | 214.74 |
| 9 | $CO+OH \rightarrow CO_2+H$ | | $4.40\ 10^{6}$ | 1.5 | −3.1 |
| 10 | $CO+HO_2 \rightarrow CO_2+OH$ | | $2.00\ 10^{13}$ | 0.0 | 96.0 |
| 11 | $CO+O_2 \rightarrow CO_2+O$ | | $1.00\ 10^{12}$ | 0.00 | 199.57 |
| 12 | $CO+O+M \rightarrow CO_2+M$[e] | $k_0$ | $1.55\ 10^{24}$ | −2.79 | 17.55 |
| | | $k_\infty$ | $1.8\ 10^{11}$ | 0.0 | 23.8 |

[a] Units are mol, s, $cm^3$, kJ, and K.
[b] Chaperon efficiencies are 2.5 for $H_2$, 16.0 for $H_2O$, 0.7 for Ar and He and 1.0 for all other species; Troe falloff with $F_c = 0.5$.
[c] Bi-Arrhenius (the sum of the two constants).
[d] Chaperon efficiencies are 2.0 for $H_2$, 6.0 for $H_2O$, 0.4 for Ar and He and 1.0 for all other species; $F_c = 0.265\exp(-T/94\text{K}) + 0.735\exp(-T/1756\text{K}) + \exp(-5182\text{K}/T)$.
[e] Chaperon efficiencies are 2.5 for $H_2$, 12.0 for $H_2O$, 2.0 for CO, 4 for $CO_2$, 0.4 for Ar and He and 1.0 for all other species; $F_c = \exp(-T/10^7\text{K}) + \exp(-10^7\text{K}/T)$.

The first 8 steps in Table 1 are the steps found in our previous work [12,15,16] to have to be retained for hydrogen autoignition. An initiation step to produce radicals from the reactants is always necessary, and this appears as step 5 in the table for hydrogen. In syngas, initiation also can occur from carbon monoxide, and that step appears as step 11 in the table. The first three entries in the table are hydrogen-oxygen chain-carrying steps (the first two chain-branching), the so-called hydrogen-oxygen shuffle reactions; there are four such elementary reactions, but, in autoignition, the fourth shuffle reaction (OH + OH ⇌ $H_2O$ + O) does not have to be retained when the first three are included. The fourth step in the table is the important step for removal of the most active radicals that carry the high-temperature hydrogen–oxygen branched-chain reaction mechanism, the mechanism that is dominant when the temperature exceeds the crossover temperature at which the rate of the fourth step is twice that of the first [17]. For syngas, in this high-temperature range, the straight-chain steps 9 and 10 need to be retained for both chemical-kinetic and energetic reasons, and step 12 becomes an important step for removing the most active radicals, like step 4. The competitions between step 3 and 9 (consumption of OH radical by $H_2$ and CO), and between steps 2 and 12 (consumption of O radical by $H_2$ and CO) are fundamental in describing the branched-chain reaction mechanism. At temperatures below crossover, the branched-chain mechanism of steps 1–3 is quenched by the dominant radical-recombination path of reaction 4, and the hydroperoxyl steps 6 and 7 then become important for producing autoignition through the generation of active radicals in step 8.