

The Effect of Solid Inhibitors on Hydrogen-air Combustion

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The use of hydrogen as an energy carrier is a promising solution for enabling the transition towards increased use of renewable energy sources in the global energy mix. However, hydrogen-air mixtures are highly reactive, and conventional technologies for explosion protection have limited applicability for hydrogen systems. As such, it is not straightforward to achieve the same level of safety for hydrogen energy systems, compared to systems based on conventional hydrocarbon fuels. The last decades have seen the development of innovative solutions for chemical inhibition of vapour cloud explosions with solid inhibitors, such as sodium bicarbonate and potassium carbonate (Roosendans and Hoorelbeke, 2019). Both substances are non-toxic, non-flammable, low-cost and relatively harmless to the environment, compared to for example halons. Although solid suppressants can be highly effective for hydrocarbons (Babushok and Tsang, 2000), experiments indicate that the same compounds are not very effective for the inhibition of hydrogen-air mixtures. The absence of carbon implies that hydrogen combustion is inherently different from hydrocarbons, however, the combustion of hydrocarbons includes the elementary reactions involved in combustion of hydrogen-air mixtures. These elementary reactions change when exposed to solid inhibitors like sodium or potassium compounds (Roosendans, 2018). Simulations of chemical kinetics based on these elementary reactions show that potassium compounds should yield a significant reduction of flame velocity. The same simulations show a significantly higher generation of radicals for hydrogen combustion compared to hydrocarbon combustion. Thus, more inhibitor is needed for effective inhibition of premixed hydrogen-air flames. For a solid inhibitor to be effective, the compound must evaporate in the flame zone, and this process appears to be the main hurdle for effective inhibition of hydrogen explosions. This paper presents results from dedicated experiments and simulations with chemical kinetics software that elaborate on previous findings and improve the understanding of the underlying mechanics of solid inhibitors in hydrogen-air combustion.

1. Introduction

As part of the transition towards increased use of renewable energy sources, hydrogen is expected to play a key role as an energy carrier. This is reflected in strategy and policy documents, as well as major investments in research and demonstration projects, by various national states and the European Union. At the same time, it is generally acknowledged that severe accidents can have significant implications for the deployment of the emerging hydrogen technologies. It is therefore of crucial importance to develop knowledge and technology that will enable stakeholders to develop hydrogen systems with an acceptable level of safety. This is not straightforward, especially for installations with high degree of congestion and/or confinement. Hydrogen-air mixtures are highly reactive and have a propensity for deflagration-to-detonation transition (DDT). This implies limited applicability of conventional methods for explosion protection, such as venting and isolation.

In this perspective, chemical inhibition of premixed hydrogen-air flames can be an effective measure of risk reduction. An ideal inhibitor would reduce the flame speed significantly, without extinguishing the flame. The reduced reactivity would enable the use of conventional methods of explosion protection and significantly reduce the probability of DDT, resulting in manageable overpressures while consuming the entire hazardous cloud.

2. Inhibitors and their effect on hydrocarbons

More than a century of dedicated research on the effect of chemical inhibitors on premixed combustion has resulted in efficient solutions for explosion protection, but primarily for hydrocarbons (Hoorelbeke, 2011). After the use of halons as fire suppressants were prohibited for environmental reasons, various metal compounds have been identified as possible replacements. Such compounds can be much more effective than halons, and the use of modern simulation tools for solving complex chemical kinetics problems have resulted in good understanding of the physical and chemical phenomena behind the inhibition effect. Recently this knowledge has successfully been used for mitigating gas and dust explosions (Rosser et al., 1963, Chelliah et al., 2003). Babushok and Tsang (2000) reviewed the state-of-the-art in chemical inhibition of hydrocarbons and developed a ranking system for the effectiveness of different inhibitors. Iron pentacarbonyl was found to be the most effective inhibitor for hydrocarbons, followed by compounds containing lead, chromium, potassium and sodium. Of these, sodium bicarbonate and potassium bicarbonate, both non-toxic and readily available, are commonly used.

3. Gaseous inhibitors and their effect on hydrogen

It is not straightforward to rank the effect of chemical inhibitors on hydrogen combustion, similar to the work by Babushok and Tsang (2000) for hydrocarbons.

Table 1 lists the most effective inhibitors identified in an experimental study by Miller et al. (1963). Notably, the best inhibitors in this study were hydrocarbons, including chlorine- or fluorine-substituted hydrocarbons. These substances are all flammable, and the main reason they perform well in this study is because the experiments were performed using rich concentrations (45 % hydrogen v/v). The hydrocarbon radical slows down the process by absorbing many of the H radicals generated in the hydrogen flame (Glassman et al., 2014).

Table 1: Laminar burning velocities of rich hydrogen-air mixtures inhibited by the ten most effective inhibitors identified by Miller et al. (1963)

Inhibitor	Laminar flame velocity (cm/s)
1,3-Butadiene	15
n-Butane	19
Ethyl chloride	25
Methane	25
Ethylene	29
Methyl chloride	31
1,1-Difluoroethane	50
Acetylene	51
Dibromotetrafluoroethane	54
Ammonia	59
None (reference)	274

Figure 1 summarises results from simulations that show that this process is most pronounced for rich hydrogen-air mixtures, with a limited supply of oxygen. The figure is produced using the GRIMECH3.0 model (Smith et al., 2017) in Cantera (Goodwin et al., 2021). The simulation results are in line with the experimental results of Miller et al. (1963). At lean concentrations, the laminar burning velocity increases somewhat when hydrocarbons are added, but the addition of hydrocarbons to hydrogen will significantly reduce the burning velocity of high concentrations. Whether this would provide an overall decrease in risk has not been assessed in this work. An assessment would be required to be able to rank flammable against non-flammable inhibitors.

Other liquid or gaseous inhibitors worth mentioning include iron pentacarbonyl and halons. While not as effective at rich concentrations, iron pentacarbonyl is effective for all concentrations of hydrogen-air mixtures (Miller et al., 1963). Halons, especially those containing iodine and bromine, also have a good inhibition effect on hydrogen-air combustion (Butlin and Simmons, 1968).

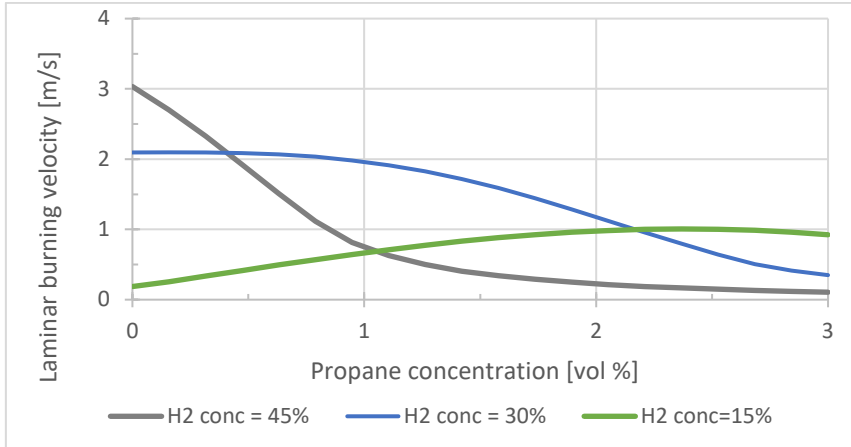


Figure 1: Simulated laminar burning velocity for lean, stoichiometric and rich hydrogen-air mixtures with added propane.

4. Solid inhibitors and their effect on hydrogen

For hydrocarbons, solid inhibitors such as potassium carbonate, potassium bicarbonate and sodium bicarbonate are widely used. These inhibitors are among the best performing inhibitors and are non-toxic. From a chemical kinetics perspective, these inhibitors should also be suitable for hydrogen. For both hydrocarbon and hydrogen combustion, consuming elementary reactions with the alkali ion become the most sensitive (Roosendans, 2018). However, experimental attempts have so far failed to confirm this theory, even though they can be quite effective for highly reactive hydrocarbons such as acetylene (van Wingerden and Hoorelbeke, 2011). The experimental data is however limited, and this observation may be related to the experimental setup.

It is well-known for solid inhibitors that the particle size distribution and residence time of the particle in the flame front is crucial (Wangsholm, 2012). For most hydrocarbons the most effective particle size lies between 10 and 30 μm . Particle sizes above 30 μm yield a weaker inhibition while particles sizes smaller than 10 μm often do not yield an additional benefit. To get a better understanding of the impact of the particle size distribution, Dounia et al. (2021) proposed a simple model that considers a uniform cloud of spherical particles heated by a one-dimensional planar flame front. Radiation from the flame is neglected and the particle is assumed to have a uniform temperature and density. Using a Lagrangian formulation for the molecular motion yields the following expression for the temperature T_s of the particles:

$$\frac{dT_s}{dt} = (T_g - T_s) (C_{p,g}/C_{p,s}) / \tau_h \quad (1)$$

where τ_h is the time scale for conductive heat transfer:

$$\tau_h = (\rho_s d_s^2 Pr) / (6 \mu_g Nu) \quad (2)$$

and T_g is the temperature of the gas, $C_{p,g}/C_{p,s}$ is the ratio of gas to particle calorific capacities, (Eq 2.), ρ_s is the density of the solid particles, d_s is the particle diameter, μ_g is the gas viscosity, Pr is the Prandtl number and Nu is the Nusselt number.

The temperature profile of a 1D-flame is calculated using a chemical solver, in this case Cantera with the GRI-Mech 3.0 model. Using the simulated temperature profile, the temperature of the particles can be calculated. Figure 2, Figure 3 and Figure 4 show the temperature profiles for stoichiometric methane-air, acetylene-air and hydrogen-air mixtures, respectively. These figures also include the temperature profile of a cloud of 50 g/m^3 potassium carbonate particles with a particle size of 10 μm . The dotted line in the graphs indicate where the amount of H radicals is at its peak. For the metal radicals to be available as radical scavengers, the solid particles need to decompose or sublimate. Thus, the particles will need to reach the decomposition/sublimation temperature in the pre-heat zone before the dotted line. For potassium carbonate, this happens at around 900 $^\circ\text{C}$ (Lehman et al., 1998) (indicated by the cross in the figures). For both the methane and acetylene flame front, the particles reach the critical temperature, while this is not the case for hydrogen. Even though the laminar burning velocity of acetylene is in the same order of magnitude as hydrogen, the flame front is much thicker, making it possible for the solid inhibitor to sublimate while still being in the flame front. In addition, an acetylene flame generates more radiation heat than a hydrogen flame, which contributes to heating up the particles before

they reach the flame front. This can explain the differences between hydrogen and acetylene seen in the experiments.

It should be noted that the approach outlined above is simplified and the graphs show an example with 10 μm particles. In addition to the idealised model for the heating of the particles, the sublimation/decomposition of the particles will also take time. Dounia et al. (2021) included models for the decomposition of the particles. The calculations, depending on the model used, yield critical particle diameters of 2.5 to 4 μm for the inhibition of hydrogen-air. Obtaining powders this fine and dispersing them without the particles agglomerating can be very challenging.

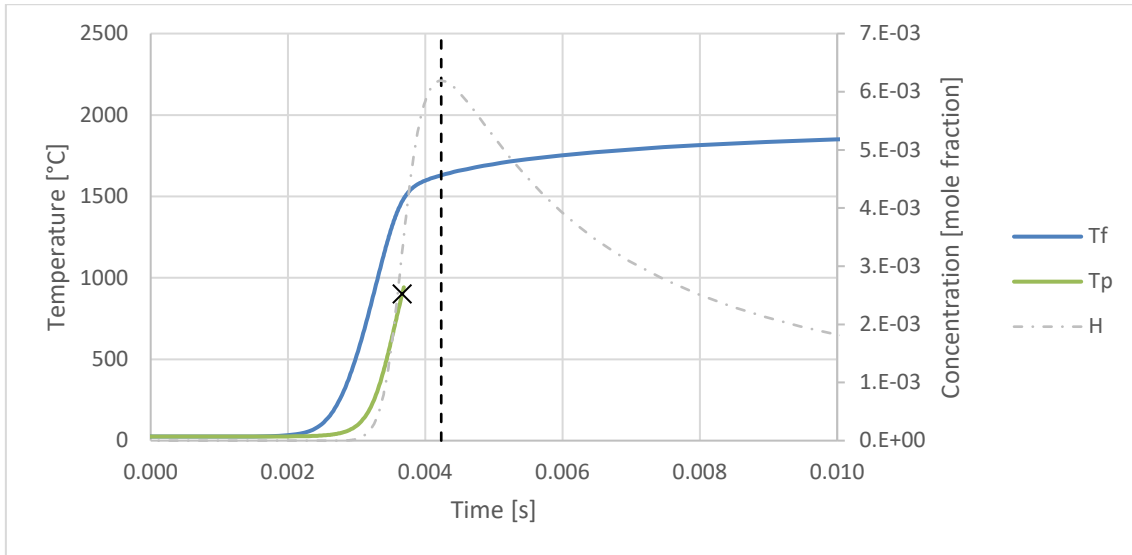


Figure 2: Temperature profile of the flame (T_f) and potassium carbonate particles of 10 μm (T_p) for a stoichiometric methane-air flame

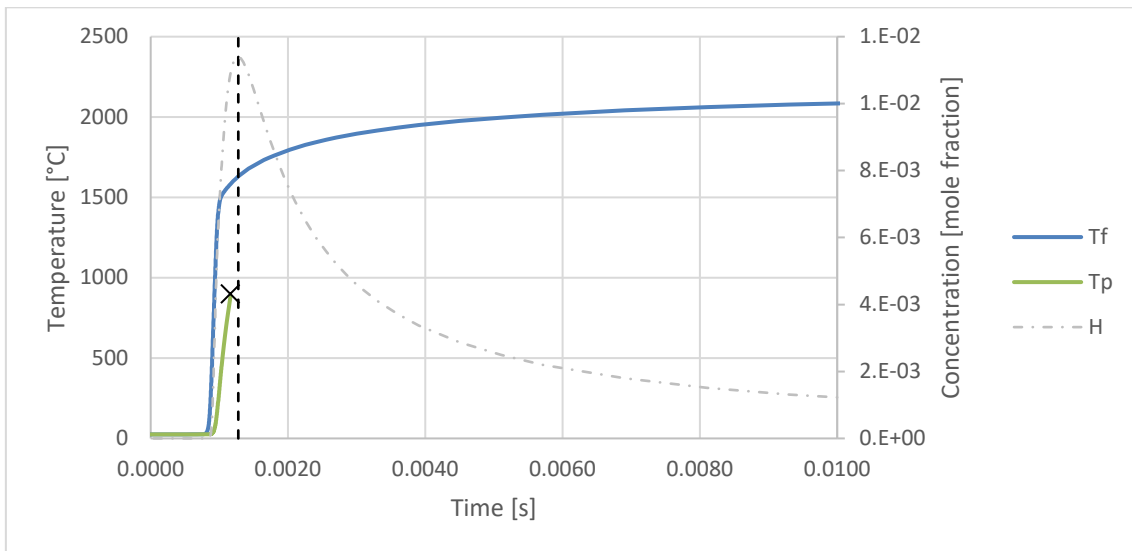


Figure 3: Temperature profile of the flame (T_f) and potassium carbonate particles of 10 μm (T_p) for a stoichiometric acetylene-air flame

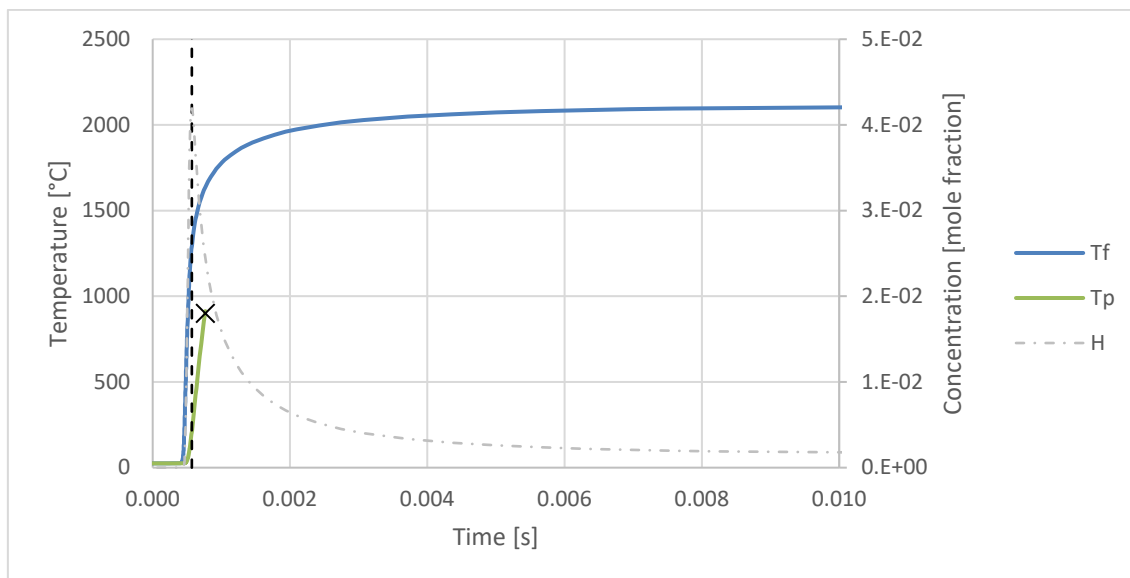


Figure 4: Temperature profile of the flame (T_f) and potassium carbonate particles of $10\ \mu\text{m}$ (T_p) for stoichiometric hydrogen-air flame

One way to overcome the issue outlined above is to dissolve the inhibitor in water. This approach can be very effective for hydrocarbons (Chelliah et al., 2002, Roosendans et al., 2017). Solutions have the potential of delivering higher concentrations of inhibitor to the flame front, but experimental results obtained with hydrocarbons indicate an upper limit for the effect of dissolved inhibitors that likely can be explained by a reduction of the flame temperature to a level where the droplets do not evaporate fast enough to deliver inhibitors in the flame zone. In addition, achieving a mist with fine enough particles can be quite challenging.

It may also be possible to identify other chemical compounds with sufficiently low melting or decomposition temperatures that can deliver metal radicals such as sodium or potassium to the hydrogen flame. Radicals from metals that have been proved in the past to be effective at recombining radicals in addition to sodium and potassium are iron, lead, manganese, chromium and tin (Linteris et al., 2008).

5. Conclusions and suggestions for further work

The increasing efforts to facilitate widespread deployment of hydrogen technologies in industry and society should be accompanied by effective solutions for explosion protection. To this end, solutions for chemical inhibition of premixed hydrogen-air flames may play a key role in reducing the consequences of hydrogen explosions, including prevention of DDT and detonations. However, a review of previous work shows that effective inhibition of hydrogen flames is not straightforward. Many of the gases and vapours identified as promising inhibitors for hydrogen are either flammable (hydrocarbons, fluorine substituted hydrocarbons), harmful for the environment (halons, fluorine substituted hydrocarbons) or toxic (iron pentacarbonyl). The main challenges of chemical inhibition of hydrogen-air flames can be explained by the high reactivity and relatively thin flame front. As a result, the carbonates and bicarbonates of alkali metals, that can be very effective inhibitors for hydrocarbons, may not be suitable for the inhibition of hydrogen when delivered as powder. An ideal solid inhibitor should have very low melting/decomposition temperature.

Further efforts to overcome the challenges associated with effective chemical inhibition of premixed hydrogen-air flames should combine fundamental experimental studies, detailed chemical kinetics simulations, and large-scale experiments for demonstration and proof of concept.

Acknowledgments

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