HYDROGEN COMBUSTION —
SAFETY HAZARDS IN HYDROGEN SYSTEMS

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ABSTRACT

Hydrogen escaping through leaks in hydrogen facility components can rapidly form a combustible mixture with the air of the surrounding atmosphere. Hydrogen/air --mixtures show a high sensitivity to ignition due to wide flammability limits and low minimum ignition energies. A combustion of the gas mixture can mean a significant danger potential due to the high temperature as well as the load imposed by the overpressure of unstationary propagating flame fronts. Since the local overpressure generally rises with the propagation velocity of a flame front, turbulent flame acceleration, which can lead to flames travelling at velocities above the speed of sound, is the key issue for the safety analysis regarding accidental combustion. In this paper the main parameters influencing flame acceleration are shortly discussed and the results of recent experiments employing non-intrusive optical measuring techniques such as laser-doppler-velocimetry and raman scattering are presented.

1. INTRODUCTION

Hydrogen is regarded as one of the most promising energy carriers of the future. Its high specific energy density and oxidation to H_2O as the main reaction product, by this not contributing to the greenhouse effect , are the main advantages. With extended use of hydrogen, more and more large hydrogen facilities such as storage tanks and distribution systems will be installed. However, hydrogen release through leaks in any part of a hydrogen facility can lead to the formation of flammable gas mixtures, especially in confined or partially confined volumes such as buildings. Small amounts of energy, i.e. sparks from electrical appliances (pumps etc.) are sufficient to ignite hydrogen/air mixtures over a wide range of mixture compositions. The flammability limits range from 4% - 74% H_2 in H_2/air [1]. If the combustion propagates as a slow deflagration, the danger potential is limited to the effects of high temperatures connected with the energy release of the chemical reaction. Turbulent flame acceleration, however, may lead to flames propagating at supersonic speeds or even escalate to detonation (DDT), i.e. [2],[3],[4]. One important characteristic of flame fronts is the strong shock wave travelling ahead of the reaction zone with peak pressures which can reach values more than one order higher than the initial pressure of the undisturbed gas. These shock waves pose a considerable danger to the regarded system, not only to installation parts but also to the surrounding buildings. Therefore safety guidelines for the design of hydrogen facilities should be established in order to minimize safety hazards due to a possible combustion.

2. COMBUSTION CHARACTERISTICS

The net chemical reaction of the combustion of hydrogen and oxygen can be expressed by the equation

$$\frac{1}{2}O_2 + H_2 \Longrightarrow H_2O + 241700kJ.$$

In reality the reaction is not a one step reaction but rather implies 28 possible steps in a pure hydrogen/oxygen mixture. In hydrogen air mixtures the presence of nitrogen adds another 41 possible reaction steps [5].

2.1. Combustion Modes

Basically there are two modes of combustion in premixed gases, the deflagration and the detonation. A deflagration propagates at low speeds relative to the unburnt gas. Heat transfer from the hot reaction zone to the unburnt gas raises the temperature of the unburnt gas until ignition occurs. The transport mechanisms involved are thermal conduction and diffusion. The speed at which a deflagration propagates into a laminar combustible mixture (laminar burnig velocity) depends only on the mixture composition, temperature and pressure of the unburnt gas.

The difference between a deflagration and a detonation is the fact that the unburnt gas in a detonation is raised to ignition temperature by a strong shock wave rather than by heat transport from the reaction zone. The extremely high rate of heat release causes a detonation to propagate at velocities far above the speed of sound. In hydrogen/air mixtures typical detonation velocities are in the order of 2 km/s. The propagation velocity of a detonation is a characteristic parameter for a combustible gas mixture, like the laminar burning velocity only depending on the initial temperature and pressure of the unburnt gas. A more detailed discussion of propagating flames is given for example in [6],[7].

The supersonic flame is not really a separate combustion mode but should be considered separately. The theory of stable propagation of supersonic flames has been introduced by Mayinger and Brehm [4]. Like in a detonation there is a leading shock, however, this shock is not of sufficient strength to cause self ignition in the mixture behind it. On the other hand, the shock causes a significant rise in temperature in the unburnt gas and therefore the actual mode of combustion is a subsonic deflagration.

For safety considerations the local overpressure caused by the combustion has to be regarded. For slow deflagrations this overpressure is rather low, for a fast deflagration it is already considerable. For supersonic flames and especially detonations, however, the overpressure is more than one order higher than the initial pressure. Fig.1 shows overpressure profiles recorded in a closed explosion tube of a fast deflagration, a supersonic flame and a detonation.

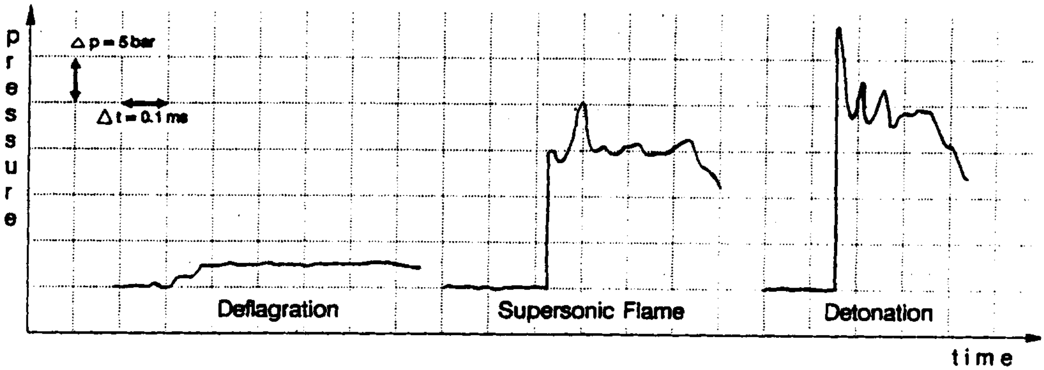

Fig. 1 : *Pressure pofiles measured at the wall of an explosion tube (stoichiometric H_2-air mixture; p_0=1 bar, T_0=296 K): a.) deflagration (flame speed: 450 m/s) b.) supersonic flame (flame speed: 1700 m/s) c.) detonation (flame speed: 2300 m/s) [10]*

2.2. Turbulent Combustion

The laminar burning velocity is a characteristic property of a combustible mixture. If the gas in which a flame propagates is not quiescent but turbulent, the flame becomes a wrinkled shape and the surface of is enlarged. In addition the heat transfer from the reaction zone to the preheat zone of the flame is enhanced. These effects cause an increase of the burning velocity with increasing turbulence. However, if turbulence within the flame zone becomes too intense local quenching effects cause a decrease of the burning velocity [4].

2.3. Turbulent Flame Acceleration

The minimum amount of energy for ignition of a slow deflagration is below 1 mJ [8]. To initiate strong deflagrations much larger ignition energies are necessary, for direct initiation of a detonation explosives rapidly releasing more than 1 kJ are necessary [9]. Therefore strong acceleration of an initially slow deflagration has to be considered the main danger source due to an accidental combustion. In (partially) confined vessels a gas flow is induced by a propagating flame due to the expansion of the combustion products. In connection with the boundaries of the vessel more or less turbulence is produced in this flow depending on the geometry of the vessel. This turbulence causes an increase of the burning velocity of the flame, thereby producing additional turbulence again. This process of flame acceleration can continue until the maximum turbulent burning velocity of the considered mixture, limited by quenching effects, is reached. The transition to a supersonic flame or a detonation can only be caused by fluidelastic instability of the flame. However this instability appears only in flames with high burning velocities [4].

An additional effect occurs in geometries that consist of several compartments connected by small openings, e.g. several rooms in a building connected by doors. After ignition in one compartment the thermal expansion of the hot gas behind the flame front causes the formation of a turbulent jet through the opening into the adjacent room. This jet not only contains unburnt gas but also partially reacted components due to turbulent mixing in the flame front and quenching effects in the highly turbulent jet flow. These partially reacted components cause elevated temperature and radical concentration in the jet and thus lead to a very rapid flame acceleration when the main flame front passes through the opening into the turbulent jet.

3. FLAME ACCELERATION: EXPERIMENTAL INVESTIGATIONS

Many experiments have been carried out in various experimental arrangements of different scale to investigate the effects of geometry and mixture composition on turbulent flame acceleration. But still no basic model for nonsteady turbulent combustion exists due to the lack of knowledge of the very complex interactions of turbulent flow and the chemical processes in the reaction front. So far successfull numerical modelling of turbulent flames has been limited to some specific problems of application.

3.1. Flame Acceleration by Jet Formation and Turbulence in H_2-air mixtures

Many investigations of turbulent flame acceleration have been conducted in explosion tubes of low diameter to length ratios. At the author's institute the influence of mixture composition and geometric parameters on combustion behaviour are investigated. The experimental setup mainly consists of a horizontal tube closed up at both ends divided into chambers by means of obstacles in the shape of orifices. The tube has a length of 6 m and a diameter of 6.6 cm. H_2 and air definitely mixtured are ignited by a spark plug located at one end of the tube. The flame velocity is measured by a photodiode system installed along the tube as shown in Fig.2.

The dependence of the flame velocity on various arrangements of the orifices was investigated with hydrogen concentrations between 10% and 30 % Vol H_2 (equivalence ratio 0.33 ... 1.0). All measurements have been conducted under constant initial conditions at 80°C(temperature) and 1 bar (total pressure). Leaner mixtures showed a low tendency to be ignited. The tube was equipped with orifices having a constant spacing over a length of 3 m beginning at the end of ignition. The spacing was varied in a range between 35 and 490 mm. Two blockage ratios of the orifices, 32% and 72%, were tested. For another series of experiments only one orifice with a blockage ratio of 72 % was mounted in the tube having a distance of 100 mm frtom the spark plug. Finally measurements were conducted in the tube without obstacles in order

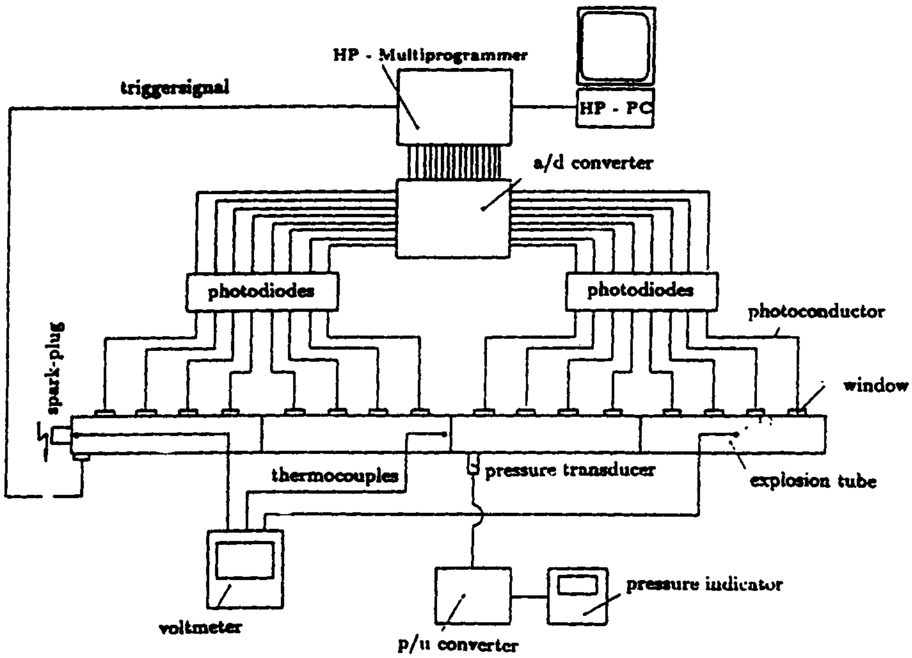

Fig. 2 : *Explosion tube with photo-diode system*

to get a reference showing the influence of the obstacles on the combustion process.

These experiments show that only few orifices are necessary for the flame to accelerate to a more or less constant maximum speed in the obstacle course. The orifices cause a jet formation with a highly turbulent shear flow into the unburnt mixture ahead of the flame front driven by the thermal expansion of the combustion products behind the flame. Even a single orifice located 100 mm from the spark plug leads to very high flame speeds. In general flame speeds decrease after the obstacle course due to the lack of turbulence generating obstructions. Only if a flame speed far beyond speed of sound is reached in the obstacle course and if the conditions for a stable detonation are met with respect to the used tube diameter (more than 20% H_2 for a diameter of 6.6 cm) a detonation propagating through the tube section without orifices is observed. The maximum flame speed reached in the obstacle course strongly depends on the spacing between the orifices and the blockage ratio. This behaviour is specific for each mixture of the chosen composition and obstacle arrangement. Flame speeds near detonation velocity were observed even in mixtures with less than 20 % Vol H_2 hydrogen. Under these, however, conditions a stable detonation cannot propagate in the used tube diameter.

Great spacings between obstacles with a high blockage ratio and obstacles with a small blockage ratio arranged with small spacings caused the highest flame

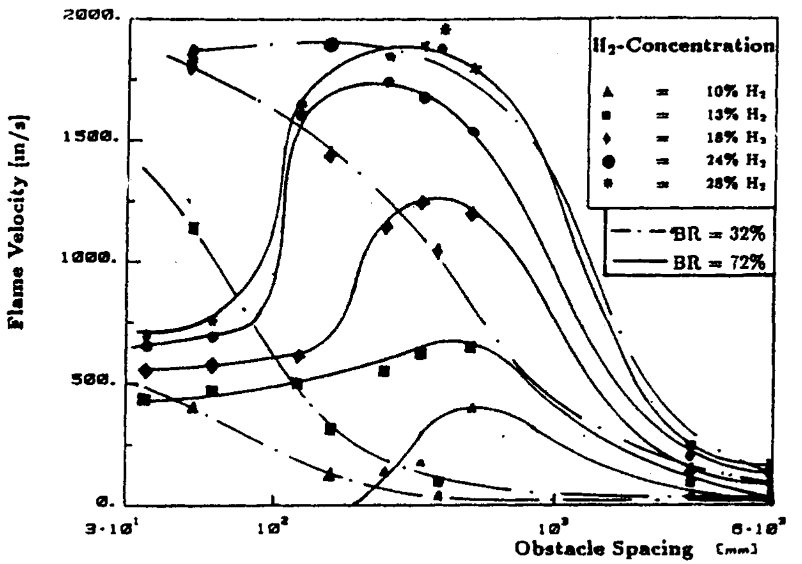

Fig. 3 : *Maximum flame velocity in the explosion tube as a function of hydrogen concentration, obstacle spacing and blockage ratio*

speeds observed for a given mixture. Fig.3 shows the maximum flame velocity in the tube as a function of concentration, obstacle spacing and blockage ratio. Obviously the orifices have two effects: First turbulence and thus the burning velocity is increased. Second in case of small spacings between obstacles with a high blockage ratio the formation of a pressure wave running ahead of the flame front necessary to reach supercritical burning velocities is prevented. Such inhibiting effects of obstructions in the flame path only have been observed in small geometries. For safety considerations in real geometries only the effect of flame acceleration is of interest. The experiments show that the combustion process not only depends on mixture composition, it is also strongly influenced by the geometric conditions. Even in very sensitive mixtures of nearly stoichiometric composition a comparatively slow deflagration can be observed in absence of obstacles. On the other hand, however, in lean mixtures down to 10% H_2 flames can be accelerated to critical speeds by means of turbulence generating obstacles.

Present investigations dealing with influence of diluent nonreactive gaseous media and elevated initial temperature on turbulent flame acceleration are still in progress. These experiments are conducted by means of the same test facility previously described. Diluents are expected to have an inhibiting effect on flame acceleration, whereas elevated initial temperature enhances the combustion process and consequently widens the range of mixture compositions for a possible transition to detonation.

3.2. Optical Measuring Techniques in Combustion Research

As shown in the previous chapter flames even in mixtures with low hydrogen content can be accelerated quite strongly under certain circumstances. However, the arrangement of obstacles in a regular pattern does not resemble the geometric conditions of any real facility. The conclusion that mixtures outside the detonability limits established by the experiments in the explosion tubes can be considered not dangerous is viable. However, these limits are very conservative with regard to volumes containing obstacles of various shape and spacing. For realistic safety evaluations models for propagating flames applicable to any given geometry are necessary. They have to include the major aspects of interaction of fluid mechanics, gas dynamics and reaction kinetics.

Probes of conventional measuring techniques, for example thermocouples or gas chromatographs, cannot be placed in any desired position without influencing the combustion process. Since in optical measuring systems the information is contained in light signals which have no effect on the investigated process, the application of optical measuring methods to combustion systems grows steadily. High local and time resolution of many optical methods are suitable for detailed investigations of the different processes involved in combustion. While for fluidmechanical properties mostly Laser-Doppler-Velocimetry (LDV) is employed, experiments concerned with measurement of temperature and species concentration, i.e. reaction kinetics, mostly rely on Rayleigh or Raman scattering, Laser-Induced- Fluorescence (LIF) or Absorption. To reveal gas dynamical effects pulsed holography can be applied. Further development of versatile lasers and sensitive light detection devices will increase the applicability of optical measuring techniques in combustion research.

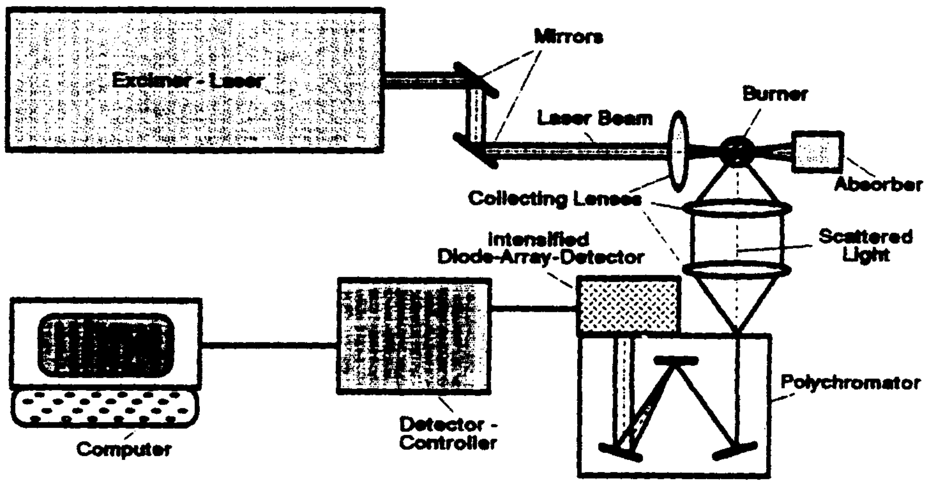

Fig. 4 : *Setup of raman scattering system*

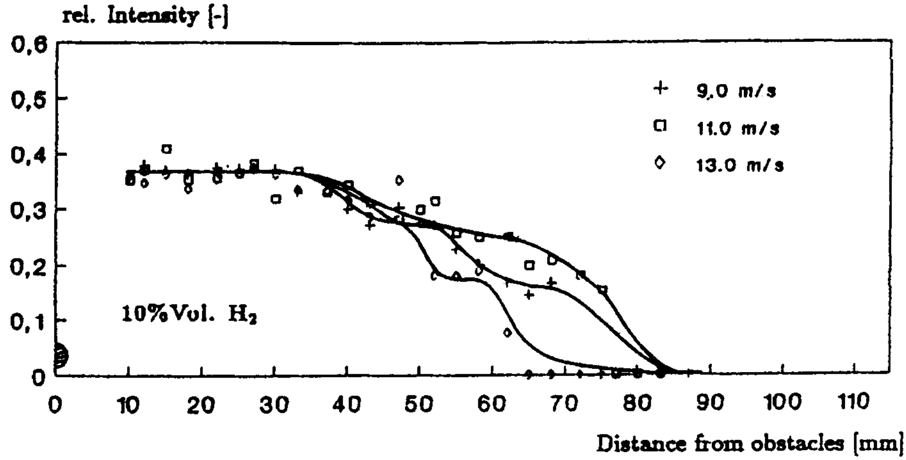

Fig. 5 : *Intensity of the H_2 raman signal (i.e. H_2 concentration) in a stationary premixed H_2-air flame downstream of turbulence inducing obstacles at initial gas velocities of 9, 11 and 13 m/s*

3.3. Stationary Flames In a Combustor with Obstacles

In order to find out more about the nature of unstationary propagating flames strongly influenced by geometric boundary conditions of the combustion vessel new methods have to be employed in this area of research. Since the flames propagate through an explosion tube in a few ms, detailed investigations in the flame region are difficult to accomplish. Therefore at the authors institute the structure of turbulent flames is examined in a stationary working tube-type burner having a rectangular cross section of 20x25 mm equipped with turbulence generating obstacles. In these projects, sponsored by the German Ministry of Research, the high energy pulsed raman scattering technique is applied to determine concentrations of hydrogen, oxygen, nitrogen and water vapor as well as temperature in the burning zone. An excimerlaser with a wavelength of λ=308nm is used as light source. The scattered light is detected by means of a polychromator and an intensified diode array detector. Fig.4 shows schematically the setup of the measuring system. A first series of experiments was recently finished with the aim of adapting the raman scattering system to the present application and developing a burner suitable to adjust different burning velocities with different mixture compositions. For these first experiments the geometric setup was held constant while the hydrogen concentration and gas velocity ahead of the flame (which is equal to the burning velocity in stationary combustion) were varied. Fig.5 shows concentration profiles of H_2 on the main axis of the burner beginning at the turbulence generating obstacle as a function of initial H_2 concentration at constant initial flow speed. Each flame exhibited a specific profile with distinct non reactive zones which can be seen from the horizontal parts of the curves. However it was not yet possible to establish a correlation of flame structure to the mixture composition and gas velocity since the turbulent flow field in the burner is unknown. The investigation of the flow field is planned using the method of laser-doppler-velocimetry (LDV).

3.4. Propagating Flames in an Explosion Tube with Obstacles

Within the framework of another project the correlations between the parameters of turbulent flow and the combustion process are investigated in the explosion tube previously described. For this purpose simultaneous measurements of the gas motion by means of a LDV system and the flame speed by means of the photodiode system are conducted. Fig.6 shows a plot of the flowspeed during a combustion experiment in the explosion tube recorded in the middle of the tube in direction of the main axis. The flame passing through the measuring volume causes a very rapid change of the flow speed. Taking into account mixture composition and initial conditions the burning velocity, meaning the speed of the flame relative to the unburnt gas, can be calculated. The fastest burning velocities observed in deflagrations reached about 70% of the critical burning velocity. Only slightly more fuel rich mixtures in connection with a given obstacle course lead to a formation of a strong shock wave propagating ahead of the flame front. The great differences between the velocities in front and behind the shock wave could not yet be measured by the LDA system. Future work will concentrate on the measurement of the turbulent flow ahead of the flame front with the aim of establishing a correlation between burning velocity and turbulence. Therefore a second component of the gas flow velocity perpendicular to the main axis of the tube will be determined.

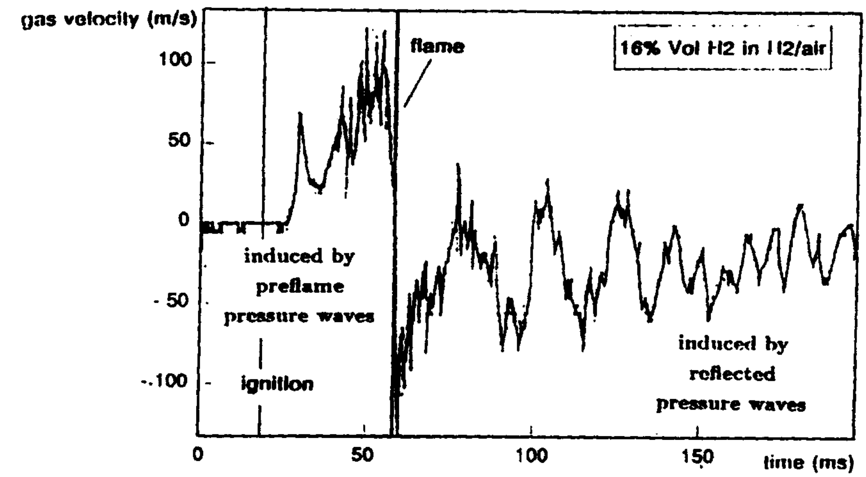

Fig. 6 : *Local gas velocity recorded in the middle of the explosion tube during a run with a premixed gas of 16% Vol. H_2 in air*

4. CONCLUSION

As hydrogen is most likely to be used more and more extensively as an energy carrier, many systems for storage, transportation and energy conversion will be developped. The rupture of any part of such a system containing hydrogen may lead to the release of large amounts of hydrogen which forms a combustible mixture with the air of the surrounding atmosphere. Considering the wide range of flamability limits and the low minimum ignition energies of hydrogen/air mixtures, a combustion is almost certain. Depending on parameters such as hydrogen concentration and geometrical boundary conditions the initially slow deflagration may be strongly accelerated up to supersonic speeds or even undergo transition to detonation. These combustion modes show high local overpressures capable of damaging installation parts or buildings of the regarded system. Therefore design rules with regard to combustion safety have to be established for the design of installations and buildings for hydrogen systems. Research conducted on unstationary hydrogen combustion up to now with a few exceptions has focussed on the behaviour of flames in various geometries. However, due to the lack of understanding the involved phenomena there are no general combustion models for unstationary combustion suitable for any given geometgry. The key to such models is more detailed knowledge about the interaction of fluid mechanics, gasdynamics and chemical kinetics. Therefore future research should concentrate on trying to establish coupling laws between these areas of interest by separating the different effects appearing in the experiments through application of appropiate measureing technique.

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