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The Influence of Diluent Gases on Combustion Properties of Natural Gas: A Combined Experimental and Modeling Study

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ABSTRACT

Currently, new concepts for power generation are discussed, as a response to combat global warming due to CO_2 emissions stemming from the combustion of fossil fuels. These concepts include new, low-carbon fuels as well as centralized and decentralized solutions. Thus, a more diverse range of fuel supplies will be used, with (biogenic) low-caloric gases such as syngas and coke oven gas (COG) among them. Typical for theses low-caloric gases is the amount of hydrogen, with a share of 50% and even higher. However, hydrogen mixtures have a higher reactivity than natural gas (NG) mixtures, burned mostly in today's gas turbine combustors. Therefore, in the present work, a combined experimental and modeling study of nitrogen-enriched hydrogen-air mixtures, some of them with a share of methane, to be representative for COG, will be discussed focusing on laminar flame speed data as one of the major combustion properties. Measurements were performed in a burner test rig at ambient pressure and at a preheat temperature T_0 of 373 K. Flames were stabilized at fuel-air ratios between about φ = 0.5 - 2.0 depending on the specific fuel-air mixture. This database was used for the validation of four chemical kinetic reaction models, including an in-house one, and by referring to hydrogen-enriched natural gas mixtures. The measured laminar flame speed data of nitrogen-enriched methane-hydrogen-air mixtures are much smaller than the ones of nitrogen-enriched hydrogen-air mixtures. The grade of agreement between measured and predicted data depends on the type of flames and the type of reaction model as well as of the fuel-air ratio: good agreement was found in the fuel lean and slightly fuel rich regime; a large underprediction of the measured data exists at very fuel-rich ratios (φ > 1.4). From the results of the present work, it is obvious that further investigations should focus on highly nitrogen-enriched methane-air mixtures, in particular for very high fuel-air ratio (φ > 1.4). This knowledge will contribute to a more efficient and a more reliable use of low-caloric gases for power generation.

Keywords: natural gas, syngas, unconventional gas, laminar flame speed, reaction mechanism, electricity generation, IGCC plant

INTRODUCTION

Over the last years, extensive efforts were assigned to the improvement of existing combustion concepts as well as to the development of new approaches for heavy duty gas turbines. Quite recently, the use of alternative and renewable energy resources was attracting much attention, besides the further reduction of pollutants and an even more increased efficiency of the overall combustion. The ultimate goal is to minimize the harmful environmental effect, with respect to emissions of CO_2, NO_x, unburnt hydrocarbons, and soot particles while maintaining security of supply, reliability, and competitiveness. A transition to a low-carbon fuel based economy is envisaged to counteract climate change caused by burning fossil fuels, *e.g.* to limit the temperature increase to less than 2°C [1]. Similar efforts are undertaken aiming to meet the energy demand in the field of road transportation [2] and aviation [3-7].

In 2011, the European Commission adopted the energy roadmap 2050 [8] for moving to a low-carbon economy, with the long-term goal of reducing greenhouse gas emissions (GHG) by 80-95% by 2050. Electricity will play a pivotal role, with the prospect of almost totally eliminate CO_2 emissions, despite the increasingly demand for power. It is interesting to note that Carbon Capture and Storage (CCS) is considered as a central low-carbon technology to achieve the EU's 2050 GHG emission reduction objectives, to be deployed after 2035.

Also in 2011, the German government has committed to an "Energiewende"- a shift from the current use of fossil fuels and nuclear power towards an energy portfolio dominated by energy efficiency as well as renewable energy. At least 80% of electricity production and 60% of primary energy need to be supplied by renewable energy sources by 2050. According to this schedule, renewables are to account for 35% of electricity production by 2020 [9] compared to 25% on average today, with values being much higher, up to 75%, during certain days.

Solid fuels (*e.g.* coal) can be burnt in heavy duty gas turbines via gasification processes or in Integrated Gasification Combined Cycle (IGCC) plants [10-15]. Applying advanced syngas combustion technology in high firing temperature engines enables to use solid fuels efficiently at low emission levels [10-14]. Further refinements are needed, *e.g.* concerning the development of highly efficient gas turbines for IGCC plants. In addition, a more comprehensive investigation of the syngas combustion technology with optimization of the burner design will widen the acceptable range in the variation of fuel composition and conditions. Thus, in combination with pre-combustion technology, an environmentally friendly exploitation of the most abundant energy source worldwide (coal) will be possible (gasification).

Improvements in fuel flexibility and load flexibility are the challenges to realize a clean production of energy. To address fuel flexibility, a wide range of different fuels will be used, such as natural gas like fuels, low-caloric fuels, hydrogen rich fuels, and biogenic gas mixtures. In particular, fuels from biomass and biomass residues can serve for an efficient and environmental friendly (almost CO_2-neutral) decentralized power generation, in micro gas turbines – with and without combined heat and power (CHP) [18-19, 26].

The composition of these gas mixtures differs considerably compared to natural gas (NG), a mixture of mainly methane, besides ethane and other lower hydrocarbons. Syngas consists primarily of hydrogen (H_2) and carbon monoxide (CO); biogenic gas mixtures of relatively high amounts of H_2 and CO, besides methane (CH_4) and inert species such as CO_2 and nitrogen (N_2); coke oven gas (COG) mostly of H_2 and CH_4, and blast furnace gases (BFG) of CO and CO_2, besides N_2.

In order to enable a reliable operation as well as the numerical simulation of combined cycles and co-firing of NG and H_2 rich gas mixtures, experimental data on laminar flame speed and ignition delay time of these gas mixtures are needed. These data may differ significantly from those of natural gas (see Fig. 1) which is burned in today's gas turbine combustors.

Hydrogen mixtures have a higher reactivity than NG mixtures: laminar flame speeds are higher, ignition delay times shorter by about one order of magnitude, and the flammability limit much broader. Thus, the propensity for auto-ignition or the occurrence of a flashback is considerably increased.

The present work reports on laminar flame speeds of hydrogen gas mixtures, with and without methane, under an enriched nitrogen atmosphere. Laminar flame speeds were measured at several fuel-air ratios, at ambient pressure, and at a constant preheat temperature T_0 = 373 K. These data were used for testing the performance of detailed reaction models. The results were analyzed concerning the combustion of natural gas.

The overall goal of the present work is to investigate the predictive capabilities of detailed chemical kinetic reaction mechanisms used previously to describe correctly combustion relevant properties of product gases from various feedstock, for a wide range of operating parameters: methane [15-16]; propene [17]; natural gas [18-20]; biogenic gas mixtures [16, 18-25]; hydrogen rich gases [16, 18-19, 21, 25], SOFC off-gases [19, 26], and co-firing of ethanol [20].

Thus, further insight will be given with respect to a more efficient and reliable use of these gas mixtures, rich in N_2 and H_2, in a gas turbine, in small and large power units.

APPROACH – EXPERIMENTAL AND MODELING

To best optimize unconventional gas mixture applications in practical combustors, their combustion characteristics, *e.g.* laminar flame speed, must be well understood.

First, measurements were performed on burning velocities S_u of two fuel-air mixtures consisting of methane and hydrogen, with a different share of nitrogen, exploiting the cone-angle method, at ambient pressure and at a preheat temperature of T_0 = 373 K: (i) methane-hydrogen-nitrogen-air-mixtures, for fuel-air ratios between 0.8 and 2.0; (ii) hydrogen-nitrogen-air-mixtures, for fuel-air ratios between 0.5 and 2.0, respectively. Details of the mixtures are summarized in Table 1.

Then, the measured data are compared with predictions using four detailed chemical kinetic reaction models, an in-house model [20] and three public-domain models [29–31]. Main features of the reaction models are summarized in Table 2. Computer simulations of the laminar premixed flames were performed with the program Chemical Workbench by Kintech Lab [32], for the assumption of a free flame. Concerning the calculations of the laminar flame speed, thermo diffusion was taken into account, to be able to model flames with high hydrogen content; for the determination of the thermal conductivity, the Dixon-Lewis method was used. Mesh points were redistributed to achieve equal solution tolerance.

It should be noted that although laminar flames have a low relevance for energy production processes, the laminar flame speed is a valuable indicator for turbulent flames, due to the strong dependency of the turbulent flame speed S_t on the laminar flame speed S_l [33]:

$$S_t/S_l = 1 + (u'/S_l)$$
$$S_t/S_l = f(Re,\ Da,\ Pr) \qquad \text{Eq. (1)}$$

u': turbulent intensity (turbulent root-mean-square velocity)

Re = Reynolds number; Da = Damköhler number; Pr = Prandtl number.

Among the fuel properties considered when qualifying a fuel for a combustion system, are the heating value - lower (H_l) and upper (H_u) - and the Wobbe index (W_l).

The heating value denotes the amount of energy released when burning a fuel, usually referring to its specific gaseous composition. For simple cycle gas turbines, the lower heating value is used since the latent energy of the water vapor in the exhaust gases is not recovered. The heating value of a fuel is a valuable information of the fuel's volume flow needed to obtain a certain power level. The volume flow is important for the proper design of fuel pipes and the burner itself.

With respect to burner design, the Wobbe index W_l is considered as an indicator for the exchangeability of gases for a certain burner. The Wobbe index is used as a parameter to indicate the ability of the overall fuel handling and injection system to accommodate the fuel composition. If the Wobbe index varies too far from the design value, changes to the fuel system need to be made. For example, for a special gas turbine, the possible relative deviation of the fuel gas' Wobbe index is given by ±5% [34], without adjustments to the fuel control system or injector flow area.

The lower Wobbe index is related to the lower heating value (Eq. 2), with density of the gaseous fuel (ρ) and of air (ρ_0), respectively, at the same temperature and pressure, as given in Eq. (3); see [35].

$$H_l = \sum_{k=1}^{n} x_k H_{l,k} \qquad \text{Eq. (2)}$$

$$W_l = \frac{H_l}{\sqrt{\frac{\rho}{\rho_0}}} \qquad \text{Eq. (3)}$$

If two different fuel gas compositions have the same Wobbe index, the pressure drop in a given fuel system will be the same for both gases; and, in general, direct substitution is possible without any changes to the fuel system required. The Wobbe index is thus an indication of energy flow in the system at the same gas pressure and pressure drop.

A high Wobbe index often indicates the presence of heavier hydrocarbons in the fuel, while a low Wobbe index is often caused by the presence of significant amounts of non-combustible fuel components or of (highly combustible) hydrogen or carbon monoxide.

EXPERIMENTAL

Burning velocities were determined for the gas mixtures given in Table 1 at ambient pressure and at a constant preheat temperature T_0 = 373 K. Data on mixtures of methane [15-16], methane/CO and CO/H_2 [18] will also be used for discussion.

All experiments were performed in our burner test rig [18; 21-24] applying the cone angle method [36].

Fuel mixtures investigated

Values of H_l and W_l of the fuel-air mixtures investigated (Table 1) in the present work were calculated (Eqs. 2 and 3) and summarized in Table 3, together with the values for other typical fuels including natural gas (NG) and the reference gas (RG) used in our group [18] to mimic natural gas.

The calculated data of the fuel-air mixtures investigated in the present work (systems I and II) are considerably lower with respect to those of natural gas, as expected. Hence, a modified burner design would be needed to burn these fuels neat.

Measurement of burning velocity

First, the experimental set-up is described followed by a presentation of the cone angle method used for determining burning velocities.

The experimental setup

A burner system was used to enable the measurement of the laminar flame speed of gas mixtures. The experimental setup (Fig. 2) consists of three major parts: (i) the burner system with the flame holder; (ii) the gas supply with the gas bottles, mass flow controllers for regulating fuel and air flows, the homogenizer to ensure a well-mixed gas mixture, temperature controllers, and the ignition system; and (iii) the detection and evaluation system. For more detailed information, refer to [18, 21-24].

Premixed conical-shaped flames have been stabilized above flame holders with nozzles of different internal diameters, to widen the kind and range of flames to be investigated. The temperature of the flame holder can be controlled between 300 and 500 K. Within the present work, for each experiment, the temperature at the nozzle's tip was measured by a type K thermocouple. This temperature agrees with the preheat temperature within less than 5 K, depending on the fuel- air ratio. Thus, we consider that heat loss to the burner has only a negligible impact in our experiment.

Recently, several fuel-air flames have been studied in our group, at pressures up to 6 bar for gaseous fuels [23] and up to 3 bar for liquid fuels, using an evaporizer [3-6].

The cone angle method

Laminar premixed flame speeds S_u were obtained by the cone angle method described in [36]. The values of S_u were derived from the visible cone angles α and the velocities v_u of the unburned gas (Eq. 4), as shown in Fig. 3a. The velocity v_u is based on the nozzle's diameter and the volumetric flow rate.

$$S_u = v_u \cdot \sin\alpha \qquad \text{(Eq. 4)}$$

In case of methane containing gas mixtures (system I), digital images of the flames were captured by a CCD camera (La Vision GmbH, Imager Intense, 1376 x 1040 Pixel) combined with a telecentric objective (Navitar Inc., 12x zoom). As flames of hydrogen-nitrogen gas mixtures free of methane (system II) are emitting too less radiation for a sensitive detection in the visible range, the flame front was visualized by OH* emission at λ = 310 nm.

Therefore, a digital camera (La Vision GmbH, Imager PRO plus 2M, 1600 x 1200 Pixel) was equipped with an UV sensitive image intensifier (La Vision GmbH, IRO, cathode S20), an UV-VIS achromatic lens (Halle Bernhard Nachfolge GmbH, focal length f = 160 mm), and an UV-passing pass filter (SCHOTT AG, DUG11). From these images, contours and cone angles α are calculated by using an edge detection algorithm.

Examples of the flames stabilized are given in Fig. 3. The overall uncertainty of the current experiments with respect to the determination of the burning velocities is estimated to be up to about ±10% for both fuel-air mixtures investigated (methane-hydrogen-nitrogen and hydrogen-nitrogen), with up to about ±15% for high fuel-air ratios ($\varphi > 1.7$). For a more detailed discussion, see [18, 21].

MODELING

The main features of the reaction models used to predict the burning velocities of the mixtures determined in the present work are given in Table 2.

Three public-domain detailed reaction models were used: (i) the GRI 3.0 [29] developed for describing the combustion behavior of methane rich gases; (ii) the Li *et al.* model [30] shown to describe the combustion behavior of syngas (hydrogen rich); and (iii) the Petrova-Williams model [31].

Also, an in-house detailed reaction model was used [20]. The DLR model is based on the RAMEC model [37] with additions concerning the sub systems of C_2H_5, C_2H_6, form- and acetaldehyde, and updates of the H_2 sub system using data given by Li *et al.* [30], as this was shown to lead to much better predictions of ignition delay times of hydrogen systems [27]. The DLR model was proven to predict ignition delay times and burning velocities of natural gas, also with addition of ethanol, as well as of syngas and biogenic mixtures [18-20].

RESULTS AND DISCUSSION

The comparison between measured and calculated laminar flame speed data of the two different sets of fuel-air mixtures will be presented (Figs. 4-6). Also, for a better understanding, burning velocities measured for mixtures of hydrogen and of a reference gas RG (92% CH_4 and 8% C_2H_6) for natural gas studied previously [18], will be discussed (Fig. 7).

The reaction models were analyzed by the use of sensitivity and rate of production analysis, to allow for a better insight into the combustion of the fuel-air mixtures studied (Figs. 8-9). For the discussion of the predictive capability of a reaction model with respect to laminar flame speed, profile shape and peak positions are valuable test parameters, besides the specific value of the laminar flame speed itself.

In summary, the predicted laminar flame speeds are in very good agreement with the measured burning velocities in the fuel lean and slightly fuel rich regime, when using the DLR reaction model and the GRI 3.0 mech. (system I, Fig. 4), with an underprediction of the experimentally determined values at high fuel-air ratios ($\varphi > 1.4$). Concerning the nitrogen enriched hydrogen-air mixtures (system II), good agreement is achieved by the use of all four detailed reaction models, with respect to absolute values as well as shape and peak position. However, measured values of the (40% H_2 - 60% N_2) fuel-air mixture are underpredicted by all reaction models in the fuel rich regime (Fig. 5), in particular by the Petrova-Williams model.

System I: Methane based fuel-air mixtures

The methane based air mixtures are consisting of a different fraction of nitrogen and hydrogen:

x H_2 / y CH_4 / (1-x-y) N_2, with x = 0.2, y = 0.2 and y = 0.5.

In total, three mixtures were studied, as pure methane-air mixtures were also considered.

The values of the measured burning velocities S_u of fuel-air mixtures of system I (Table 1) are plotted in Fig. 4 (denoted by full symbols); they were stabilized over a wide range of fuel equivalence ratio φ, within $0.80 < \varphi < 2.0$. In general, the curves are quite similar, with respect to shape and peak position. The laminar flame speed data for the mixture of pure methane are very similar – in terms of absolute values – to those of the (50% CH_4 - 20% H_2 - 30% N_2) mixture, showing slightly lower values (see Fig. 4d). This is due to the chosen amounts of hydrogen (leading to higher S_u values) and nitrogen (leading to lower S_u values) in the CH_4-H_2-N_2 mixture. Further increasing the fraction of nitrogen yields considerably lower values, by up to about 30% (peak). However, the curve's shape is not affected. The lower values of the nitrogen enriched mixtures are clearly attributed to the high share of this inert species (N_2) mixtures because mixtures with equal amounts of hydrogen and methane show values being about twice as high, with the curve's shape narrowed (Fig. 4d).

In general, a good agreement between measured and calculated data exists (Fig. 4). The reaction models considered succeed in predicting the main features (shape, trend); however, the specific values of the burning velocity S_u are underpredicted at very fuel rich ratios ($\varphi > 1.4$) by all mechanisms. Note that the measured laminar flame speed data are matched best by using the DLR reaction model and the GRI 3.0 mech., in particular in the fuel lean and slightly fuel rich regime.

The most deviations between experiment and calculations are occurring at very rich fuel-air ratios ($\varphi > 1.4$). In this regime, absolute values of laminar flame speeds are quite low, in particular for nitrogen-enriched methane-hydrogen flames. It is known that the cone angle method might be considerably affected by strain and curvature, in particular for flames fueled by a species with a high diffusivity such as hydrogen [18, 21].

System II: Hydrogen based fuel–air mixtures

Hydrogen mixtures burning in air with a different share of nitrogen (system II, see Table 1) could be stabilized over a wide range of fuel equivalence ratio φ, within $0.5 < \varphi < 2.0$ (Fig. 5, full symbols). The lower the fraction of hydrogen, the lower the measured values, with the peak value lowered by about a factor of 2.5 for a 40% share of hydrogen, compared to a pure hydrogen flame. In addition, the shape of the curve is changing dramatically, from a curve achieving a quasi-plateau level in the fuel rich regime (Figs. 5a and 5b) to a more bell-shaped curve, with a distinct maximum, similar to hydrocarbon flames (Figs. 5c and 5d).

Referring to the comparison between measured and predicted values of the burning velocities of the hydrogen rich mixtures of system II (Fig. 5, symbols - curves), very good agreement is achieved by the use of the four detailed reaction models, with respect to absolute values as well as shape and peak position. Note that measured values of the (40% H_2 -60% N_2)-air mixture are underpredicted by all reaction models in the fuel rich regime (Fig. 5d).

Discussion of system I & system II mixtures

For all mixtures studied in the present work, of system I and system II, the experimentally determined (symbols) and predicted (curves) data using the DLR reaction model [20] are combined in Fig. 6.

The huge differences in the specific values of the laminar flame speed data for these different kinds of mixtures (methane and hydrogen based, respectively) together with the differences in the curves' shape clearly demonstrate the need for a comprehensive investigation of flame characteristic properties when using hydrogen rich mixtures (syngas), in particular in existing burner or gas turbine set ups.

Similar results are obtained with respect to the combustion of natural gas, pure or enriched with hydrogen (Fig. 7). Values of laminar flame speed data are plotted as a function of hydrogen percentage, for a fuel-lean ($\varphi = 0.6$), a stoichiometric and a fuel-rich mixture ($\varphi = 1.5$). A somehow dwell percentage of hydrogen seems to exist because of the exponential increase with a hydrogen percentage larger than about 60%.

Analysis of the detailed reaction mechanisms

Sensitivity analysis were performed with respect to laminar flame speeds for a mixture of system I (Fig. 8) and of system II (Fig. 9), respectively, by using the DLR reaction model [20] and the one of Li *et al.* [30]. Results (normalized local sensitivity) are given for three fuel-air ratios: fuel-lean ($\varphi = 0.6$); stoichiometric, and fuel-rich ($\varphi = 2.0$).

In summary, the patterns are quite similar, for the same mixture and the reaction models used. In both systems, the burning velocities are mostly sensitive to the kinetics of the chain branching reaction $H+O_2=OH+O$ followed by reactions pertaining to the H/O- sub-system (only, for mixture of system II, Fig. 9) as well as CO-sub-system and methyl (for mixture of system I, Fig. 8). Reactions involving H atoms become more important with higher values of the fuel-air ratio, and even more, when a hydrocarbon (methane) is included. Recombination reactions such as $H+O_2=HO_2$ are more important in the fuel lean regime, due to the high amount of molecular oxygen. These results reflect the need of using accurate H/O and C/O sub systems. In contrast, recombination reactions of H atoms with hydrocarbon radicals are more important in the fuel-rich regime.

CONCLUSIONS

Improvements in fuel flexibility and load flexibility are the challenges to realize a clean production of energy, strongly related to concepts of power generation. Reliable data of major combustion characteristics like laminar flame speeds are needed, under a wide range of relevant parameters.

In the present work, laminar flame speeds of different hydrogen gas mixtures, with and without methane, under enriched nitrogen atmosphere, were measured at ambient pressure and elevated temperatures (T_0 = 373 K), for different fuel-air ratios. The huge differences in the specific values of the laminar flame speed data for these different kinds of mixtures (methane and hydrogen based, respectively) together with the differences in the curves' shape clearly demonstrate the need for a comprehensive investigation of flame characteristic properties when using hydrogen rich mixtures (syngas), in particular in existing burner or gas turbine set ups.

Laminar flame speeds were predicted by four detailed reaction models including an in-house one. For the nitrogen-enriched methane-hydrogen-air mixtures (system I), very good agreement with the measured burning velocities were found in the fuel lean and slightly fuel rich regime, when using the DLR reaction model and the GRI

3.0 mech., with an underprediction of the experimentally determined values at very fuel-rich ratios ($\varphi > 1.4$). For the nitrogen-enriched hydrogen-air mixtures (system II), good agreement is achieved by all four detailed reaction models. However, measured values of the (40% H_2 - 60% N_2) air mixture are underpredicted by all reaction models in the fuel rich regime.

From the results of the present work, it is obvious that more data are desirable for very high fuel-air ratio ($\varphi > 1.4$), where the largest deviations between experiment and calculations exist. In this regime, absolute values of laminar flame speeds are quite low, in particular for nitrogen-enriched methane-hydrogen flames. In general, further investigations should be done for highly nitrogen-enriched fuel air mixtures. This knowledge will contribute to a more efficient and a more reliable use of low-caloric gases for power generation.

Nomenclature

p	Pressure
t	Time
T	Temperature
H_l	Lower heating value
H_u	Upper heating value
W_l	Heating index
S_u	Laminar flame speed
Da	Damköhler number
Pr	Prandtl number
Re	Reynolds number
v	Velocity of gas mixture

Greek letters

α	Cone angle

λ	Wavelength
φ	Fuel equivalence ratio
τ	Ignition delay time
ρ	Density

Subscripts

0	initial
l	laminar
t	turbulent
ign	Ignition
u	unburnt

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Table 1 **Fuel-air mixtures studied in present work**

Fuel	Share / vol% mol fraction			Burning velocity S_u measured at T_0 = 373 K and p = 1 bar	
	H_2	N_2	CH_4, NG *for B*	Fuel-air ratio φ	*Ref.*
A. *Present Work*					
System I: Methane based					
CH_4	0	0	100	0.9 – 2.0	*p.w.*
	20	60	20	0.8 – 2.0	
	20	30	50	0.8 – 2.0	
System II: Hydrogen based					
H_2	100	0	0	0.5 – 2.0	*p.w.*
	80	20	0	0.5 – 2.0	*p.w.*
	60	40	0	0.5 – 2.0	*p.w.*
	40	60	0	0.5 – 2.0	*p.w.*
B. *For comparison*					
Natural Gas	0	0	100	0.85 – 1.3	[18]
(92%CH_4	25	0	75	0.85 – 1.8	[18]
+8%C_2H_6)	50	0	50	0.70 – 2.0	[18]
	65	0	35	0.70 – 2.0	[18]
	80	0	20	0.70 – 2.0	[18]

Table 2 Detailed chemical kinetic reaction models used

Reference	Species	Reactions
DLR [20]	65	398
GRI 3.0 [29]	53	325
without N sub model	36	219
Li *et al.* [30]	21	91
Petrova, Williams [31]	46	235

Table 3 Calculated data at $T = 273$ K for heating values (H_l, H_u) and Wobbe index (W_l) of fuels considered

Fuel \ Value@ T = 273 K	$H_{u,\ higher}$ / MJ m^{-3}	$H_{l,\ lower}$ / MJ m^{-3}	W_l / MJ m^{-3}
A. *Present work*			
System I: Methane based			
Methane	39.73	35.80	48.12
+ 20% H_2+30% N_2	22.42	20.06	26.32
+ 20% H_2+60% N_2	10.50	9.32	11.10
System II: Hydrogen based			
Hydrogen	12.77	10.80	40.93
+ 20% N_2	11.21	8.64	17.31
+ 40% N_2	7.66	6.48	9.90
+ 60% N_2	5.11	4.32	5.54
B. *For comparison*			
Syngas - 50% H_2+50% CO	12.7	11.71	16.27
Natural Gas	35-50		40-50
92% CH_4 -8% C_2H_6 - (RG)	42.12	38.03	49.42
90% RG +10% ethanol*	44.19	39.94	48.01
Ethanol*	62.9	57.16	45.33
Biogenic gas I - corn [23]	30.27	27.17	39.72
Biogenic gas II - wood [18]	5.31	4.91	5.21
Biogenic gas III - algae [18]	22.90	20.64	21.84

*: Values of ethanol are based on (vaporized) gaseous state.

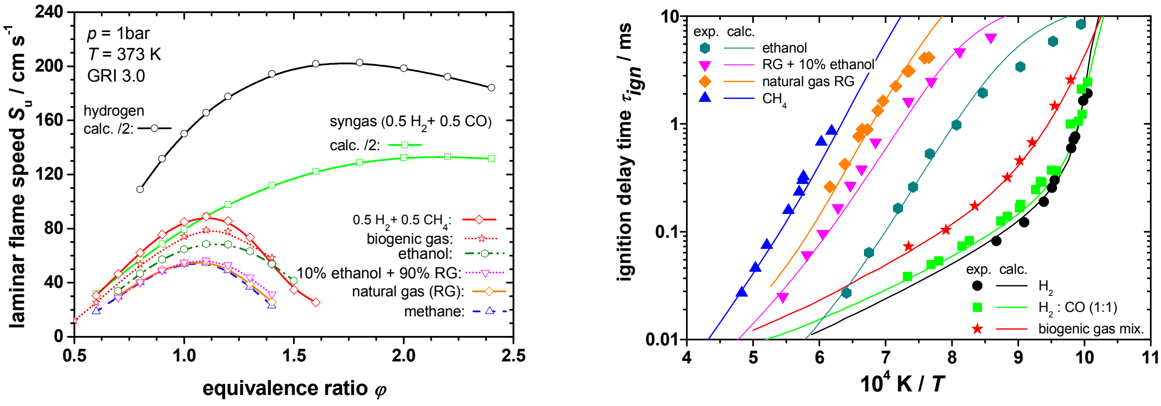


Fig. 1 Characteristic combustion properties. Left: Laminar flame speeds of fuel-air mixtures at p = 1 bar, T_0 = 373 K. Calculations (curves) for: methane, natural gas, syngas, biogenic gas: GRI 3.0 [29]; for ethanol, (10% ethanol + 90% RG): DLR [20]. Right: Ignition delay times measured (symbols) and predicted (curves, DLR reaction model [20]) of fuel-air mixtures diluted in argon 1:5 at φ = 1.0, p = 4 bar, oxidizer: 79% Ar-11% O_2. Fuel: H_2 [27] – circles, black; 50% H_2 - 50% CO [28] – squares, green; biogenic gas [18] –stars, red; ethanol [20] – dark blue, diamond; RG+10% ethanol [20] – magenta, triangles down; natural gas [27] – rhombs, orange; CH_4 – triangles, blue.

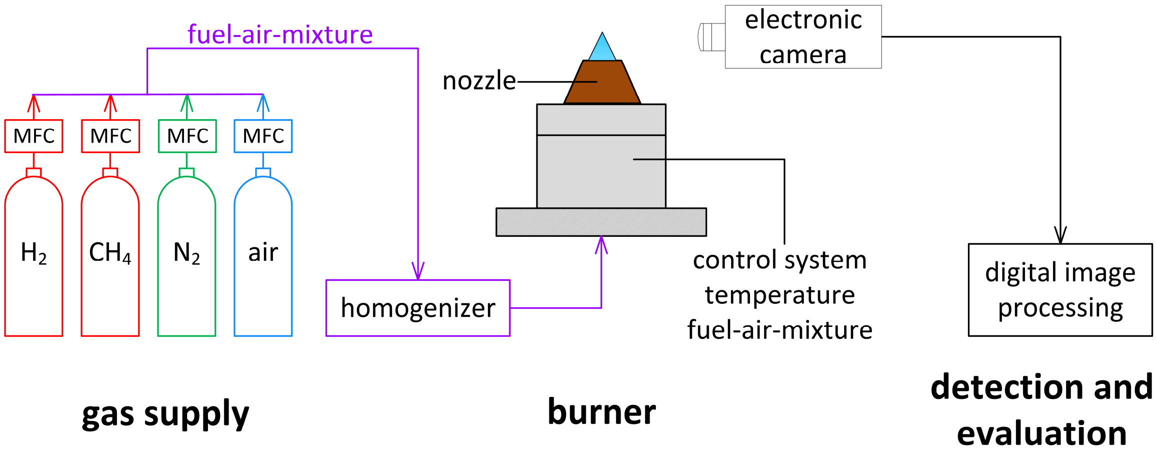


Fig. 2 Experimental setup of the burner system

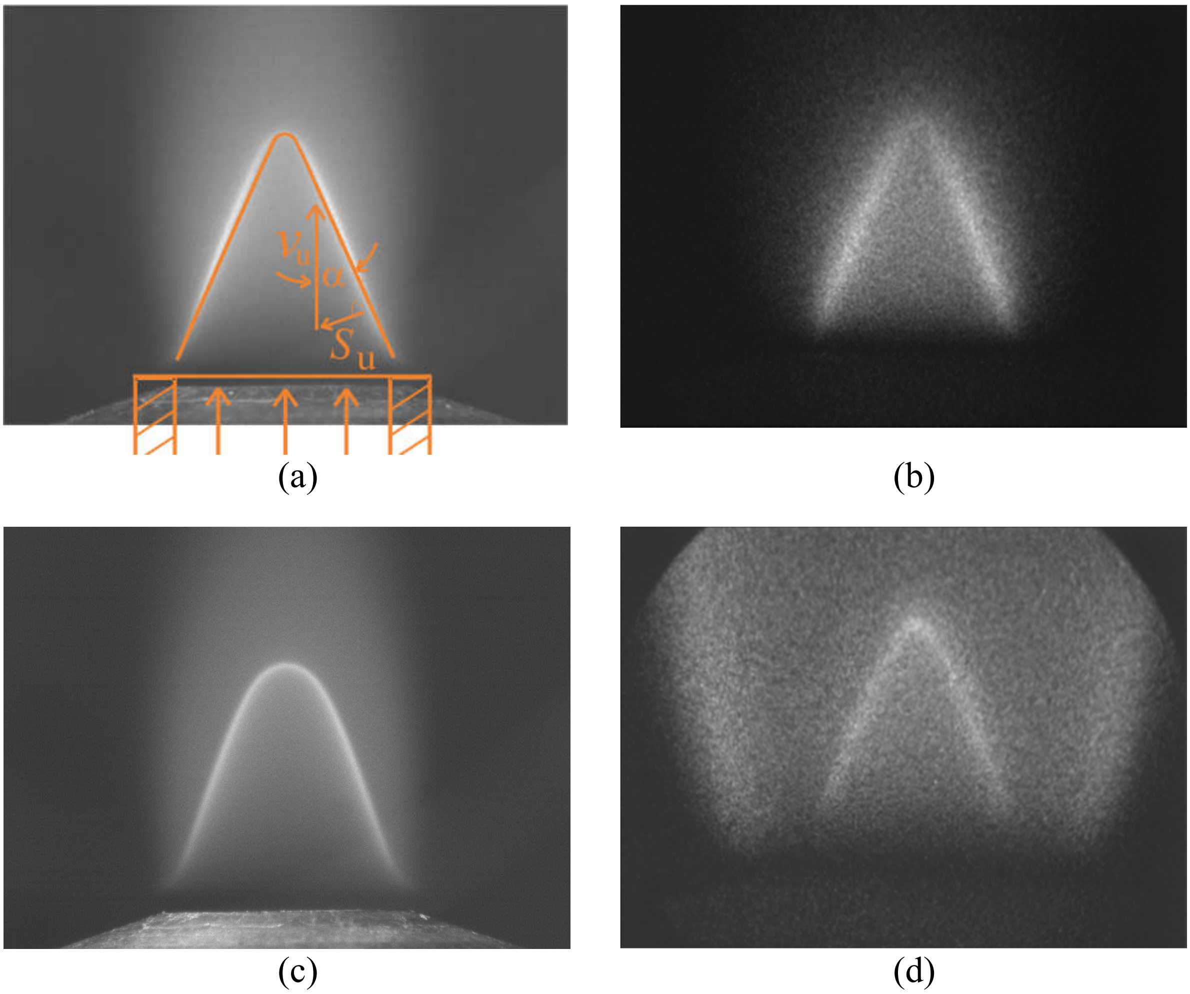
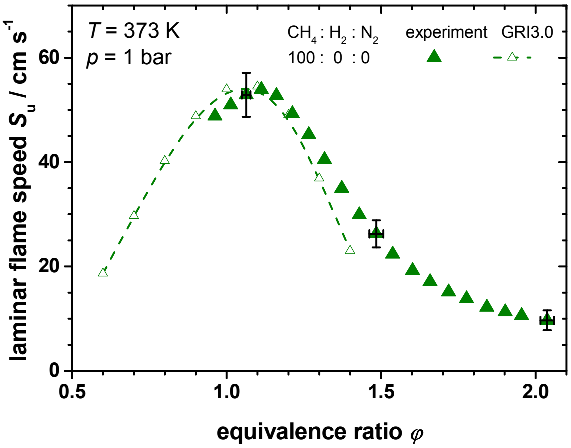
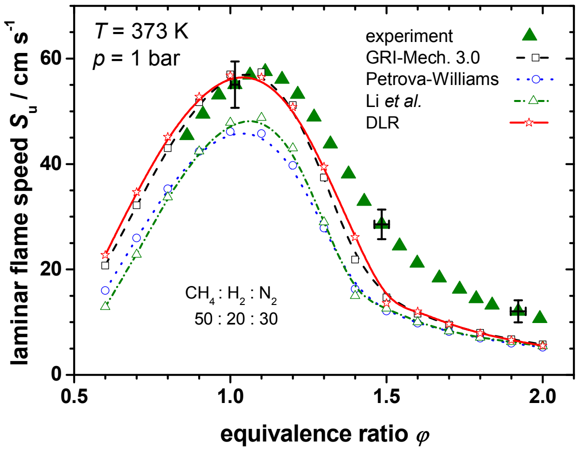


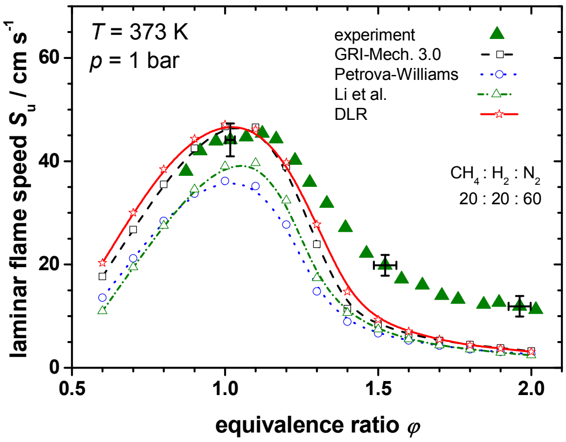
Fig. 3 Typical flames burned in air at p = 1 atm and T_0 = 373 K, for two fuel-air mixtures: 20% CH_4 - 20% H_2 - 60% N_2 (a, c); 80% H_2 - 20% N_2 bar (b, d). Fuel-air ratio: φ = 1.12 (a); φ = 1.01 (b); φ = 1.39 (c); φ = 2.03 (d)



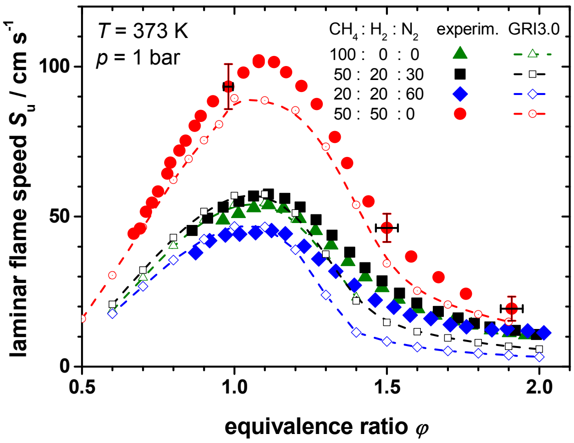
(a)



(b)



(c)



(d)

Fig. 4 Comparison between measured burning velocities (symbols) and calculated laminar flame speeds (curves) of fuel-air mixtures of system I, at p = 1 bar and T_0 = 373 K. Fuel: 100% methane – (a); 50% CH_4 - 20% H_2 - 30% N_2 – (b); 20% CH_4 - 20% H_2 - 60% N_2 – (c); 50% H_2 - 50 % CH_4 and all 3 mixtures given before – (d). Calculations with reaction models of: DLR [20] - full, red; GRI 3.0 [29] - dashed, black; Li *et al.* [30] - dash-dotted, green; PeWi [31] - dotted, blue

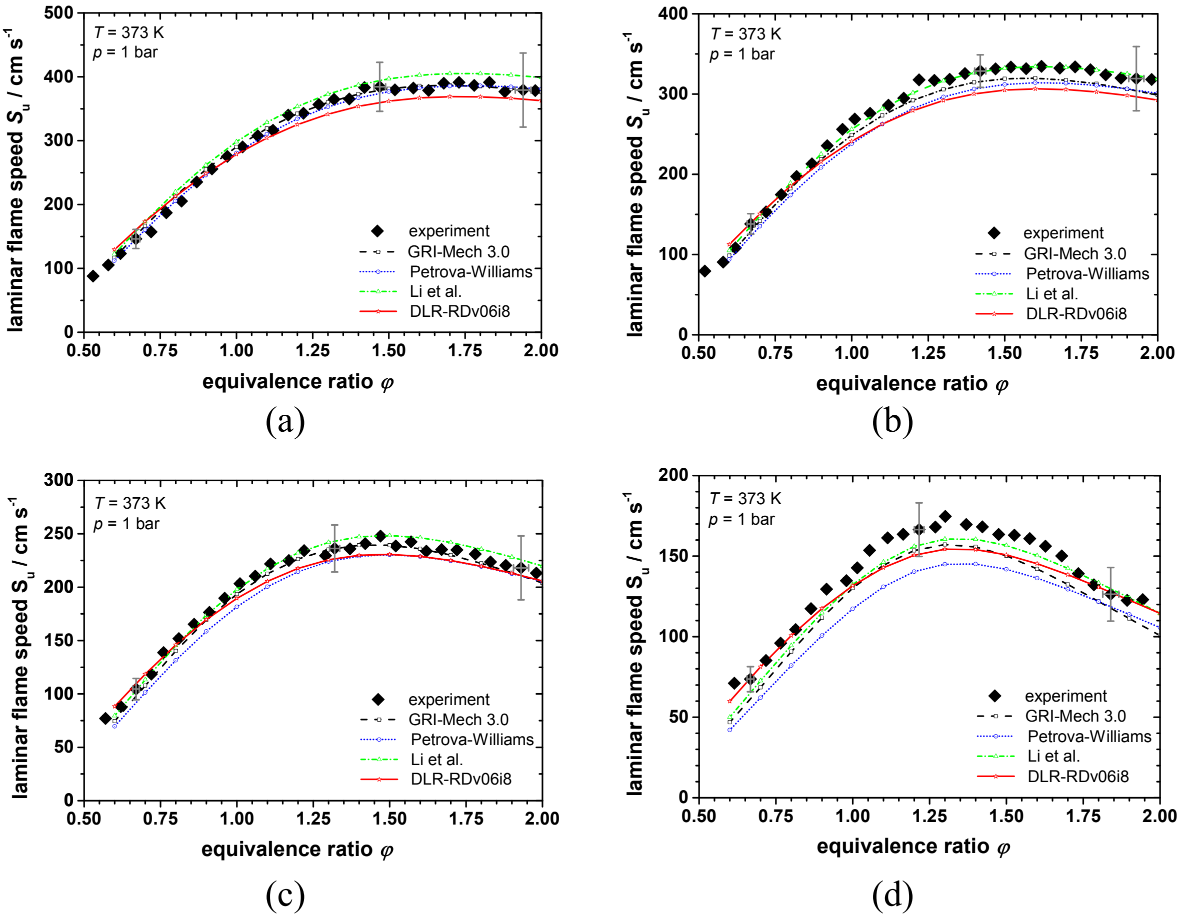


Fig. 5 Comparison between measured burning velocities (symbols) and calculated laminar flame speeds (curves) of fuel-air mixtures of system II, at p = 1 bar and T_0 = 373 K. Fuel: 100% H_2 – (a); 80% H_2 - 20% N_2 – (b); 60% H_2 - 40% N_2 – (c); 40% H_2 - 60% N_2 – (d). Calculations with reaction models of: DLR [20] - full, red; GRI 3.0 [29] - dashed, black; Li *et al.* [30] - dash-dotted, green; Pe-Wi [31] - dotted, blue

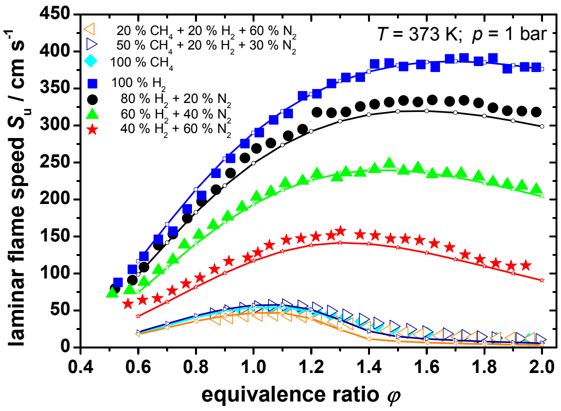


Fig. 6 Comparison between measured burning velocities (symbols) and calculated laminar flame speeds (curves; DLR reaction model [20]) of two fuel-air mixtures (systems I and II), at p = 1 bar and T_0 = 373 K

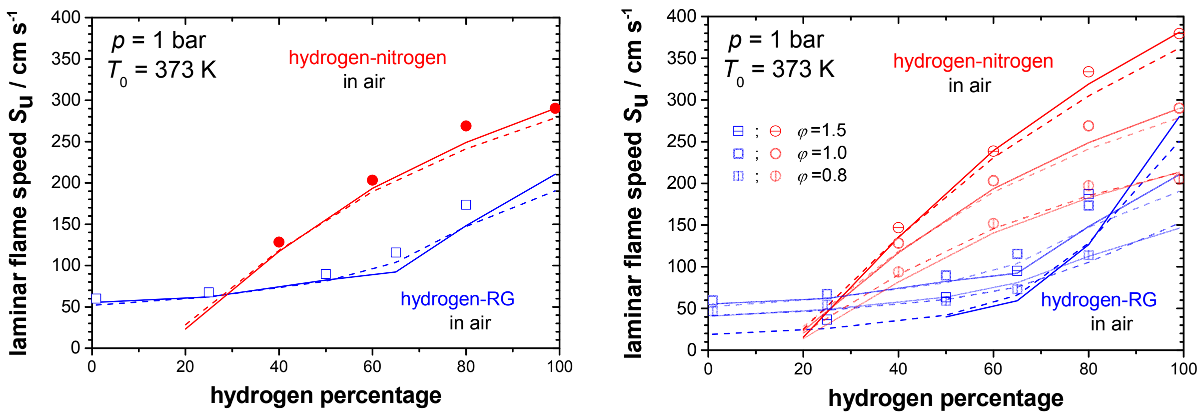


Fig. 7 Comparison between measured burning velocities (symbols) and calculated (curves) laminar flame speeds of two fuel-air mixtures (system II, and H_2-RG [18]), at p = 1 bar and T_0 = 373 K. Calculations with reaction models of: DLR [20] – full; GRI 3.0 [29] – dashed. Fuel-air ratio φ = 1.0 (left); φ = 0.8; 1.0; 1.5 (right)

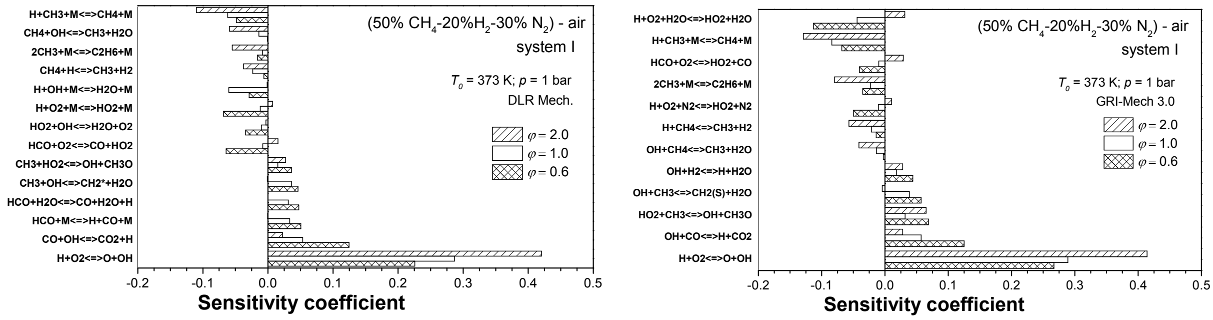


Fig. 8 Sensitivity analysis with respect to laminar flame speed of a (50% CH_4 - 20% H_2 - 30% N_2)-air mixture (system I), for three fuel-air ratios. Calculations with reaction models: DLR [20] – left; GRI 3.0 [29] – right

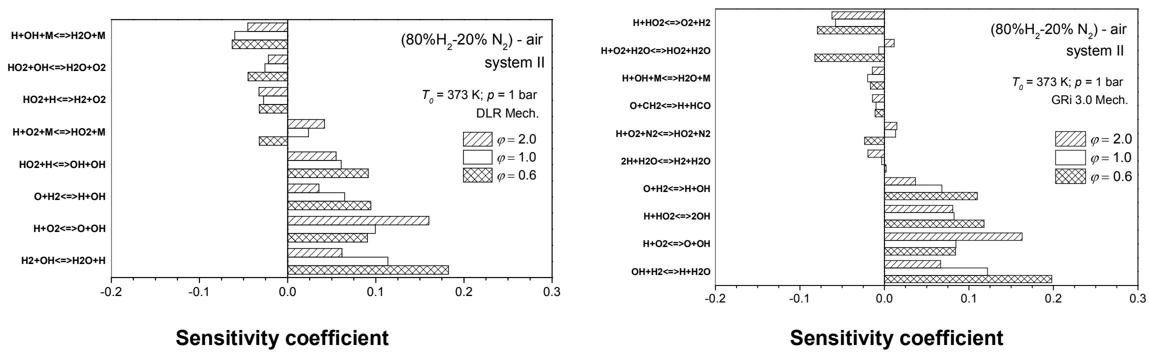


Fig. 9 Sensitivity analysis with respect to laminar flame speed of a (80% H_2-20%N_2)-air mixture (system II), for three fuel-air ratios. Calculations with reaction models: DLR [20] – left; GRI 3.0 [29] – right