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Alternative Fuels based on Biomass: An Experimental and Modeling Study of Ethanol Co-firing to Natural Gas

Marina Braun-Unkhoff, Jens Dembowski, Jürgen

Herzler, Jürgen Karle, Clemens Naumann, Uwe Riedel

German Aerospace Center (DLR)

Institute of Combustion Technology

Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

E-Mail: Marina.Braun-Unkhoff@dlr.de

ABSTRACT

In response to the limited resources of fossil fuels as well as to their combustion contributing to global warming through CO_2 emissions, it is currently discussed to which extent future energy demands can be satisfied by using biomass and biogenic by-products, *e.g.* by co-firing. However, new concepts and new unconventional fuels for electric power generation require a re-investigation of at least the gas turbine burner if not the gas turbine itself to ensure a safe operation and a maximum range in tolerating fuel variations and combustion conditions. Within this context, alcohols, in particular ethanol, are of high interest as alternative fuel. Presently, the use of ethanol for power generation - in decentralized (micro gas turbines) or centralized gas turbine units, neat, or co-fired with gaseous fuels like natural gas and biogas - is discussed. Chemical kinetic modeling has become an important tool for interpreting and understanding the combustion phenomena observed; for example, focusing on heat release (burning velocities) and reactivity (ignition delay times). Furthermore, a chemical kinetic reaction model validated by relevant experiments performed within a large parameter range allows a more sophisticated computer assisted design of

burners as well as of combustion chambers, when used within CFD (computational fluid dynamics) codes. Therefore, a detailed experimental and modeling study of ethanol co-firing to natural gas will be presented focusing on two major combustion properties within a relevant parameter range: (i) ignition delay times measured in a shock tube device, at ambient (p = 1 bar) and elevated (p = 4 bar) pressures, for lean (φ = 0.5) and stoichiometric fuel-air mixtures, and (ii) laminar flame speed data at several preheat temperatures, also for ambient and elevated pressure, gathered from literature. Chemical kinetic modeling will be used for an in-depth characterization of ignition delays and flame speeds at technical relevant conditions. An extensive database will be presented identifying the characteristic differences of the combustion properties of natural gas, ethanol, and ethanol co-fired to natural gas.

Keywords: co-firing, ethanol, natural gas, ignition, laminar flame speed, reaction mechanism, decentralized electricity generation

INTRODUCTION

Presently, the largest part of our energy used - electric power generation, heating, transportation, and aviation - is based on fossil fuels. In the last decade, alternative and renewable energy resources became increasingly important, mainly to combat greenhouse emissions, but also to ensure security of supply and a lower increase of costs for energy by reducing fuel import dependency.

Sustainability in energy supplies requires new concepts with respect to feedstock, production, and the final product. Improvements in overall-efficiency of the technical process are desirable as this will directly lead to lower emissions of CO_2, besides NOx, unburned hydrocarbons, and soot particles, thus contributing towards an environmental friendly energy production.

To meet the expected increase of the electrical power demand by annual 2.2% worldwide until 2035 [1], additional power plant resources must be provided. An increase in efficiency and at the same time a reduction of CO_2 and pollutants is required. Therefore, a variety of fuels will be burned, ranging from natural gas like fuels to

“altogether fuels”. Small to large-scale gas turbines - stand alone, process integrated or in combined cycles - will also be needed.

Renewable fuels have a large potential for power generation, besides for road transportation [2] and aviation [3-5]. Fuels from low quality feedstock such as biomass and biomass residues are burned, including low caloric and hydrogen rich fuels [6]. Detailed knowledge of fundamental combustion properties such as laminar flame speed and auto ignition [7-8] is a prerequisite to enable a reliable and safe operation with low emission characteristics, for example with respect to the concept of co-firing natural gas and biogenic gas mixtures.

Within this context, micro gas turbines offer several advantages over conventional gas engines, such as high fuel flexibility with a broad range of liquid and gaseous fuels [9] and substantially lower pollutant emissions. Their on-site combined heat and power production are expected to play a more prominent role in the near future, in particular for decentralized power generation [10, 11]. An increase of the electrical efficiency of small gas turbines to more than 50% can be reached following the idea of a hybrid power plant [12].

For the reasons mentioned above, alcohols have gained high interest as alternative fuel and fuel additive. Besides their potential of a CO_2-neutral energy source, they can also inhibit the formation of polyaromatic hydrocarbons (PAH) and soot [13] and improve overall engine performance [14]. Ethanol can be produced from renewable sources which contain starch, sugar or cellulose, mostly by fermenting sugar or by converting starch, from common crops, such as sugar cane, sugar beet waste and molasses, or corn and corn cabs. Ethanol, a “first-generation” biofuel plays a major role within the transport sector due to its widely use in vehicular applications, in particular in Brazil [15]. Quite recently, producing renewable synthetic jet fuels from sugar known as alcohol to jet (ATJ) and sugar to jet (STJ) became possible [16].

However, the use of alcohols for power generation is also discussed, with ethanol being the most prominent one: Burning in centralized gas turbines or decentralized micro gas turbines, neat, or co-fired, with liquid fuels like diesel or kerosene or gaseous fuels like natural gas and biogas.

Higher alcohols, such as butanol, pentanol, and hexanol, offer several advantages compared to smaller ones (methanol, ethanol), with higher energy density, reduced evaporative emissions, lower hygroscopicity, lower vapor pressure, and reduced corrosiveness being among them[14]. Thus, an increased use of higher alcohols is foreseen in the future. However, the production and use of these so-called "next-generation" alcohols is still under development.

In this context, chemical kinetic modeling has become an important tool for interpreting and understanding the combustion phenomena observed. Due to the hierarchical structure of a chemical kinetic reaction model, the understanding of the combustion mechanism of small alcohols is very important for the ones of higher alcohols. The oxidation of all these higher compounds proceeds through the same decomposition/oxidation steps. For example, ignition delay data are very important for the development and validation of reaction mechanisms because they describe the global reactivity of the fuel at various mixture compositions, temperatures, and pressures [14].

Hence, the goal of the present work is twofold: (1) to provide combustion relevant properties of ethanol and ethanol/natural gas mixtures for a wide range of parameters by creating a comprehensive data set to enable an optimized combustor design; (2) to investigate the performance of detailed chemical kinetic reaction models as they become increasingly relevant for predictive CFD simulations of technical combustors, and to support the optimization of *e.g.* micro gas turbine combustion design.

Ignition delay times were measured in a shock tube device, at ambient (p = 1 bar) and elevated (p = 4 bar) pressures, for lean (φ = 0.5) and stoichiometric (φ = 1.0) fuel-oxygen mixtures (diluted with argon) usually chosen to cover the most relevant fuel-air ratios when burning a fuel in a gas turbine, for validating a detailed reaction model [6, 22]. Laminar flame speed data are gathered from literature [17-18] for several preheat temperatures, also for ambient and elevated pressures. To find out if the fundamental combustion properties considered may differ significantly, additional studies performed in our group on gas mixtures of several fuels [6] are also taken into account.

Thus, as the ultimate goal, a validated chemical kinetic reaction model will be provided as a prerequisite to models used in CFD simulations for a more efficient burner and combustor design process.

Fig. 1

Characteristic combustion properties. Left: Laminar flame speeds of different fuel-air mixtures, p = 1 bar, T_0 = 373 K. Experiments –50%H_2/50% methane mixture [8]; calculations (curves) with a detailed reaction model, GRI 3.0 [20]. Right: Ignition delay times of different fuel-air mixtures diluted in argon 1:5. Comparison between experiment (symbols) and calculations (curves, with DLR-RG reaction model, *p.w*) for: φ = 1.0, p = 4 bar, oxidizer: 79% Ar, 21% O_2. Black: H_2 [21]; green: 50% H_2/ 50% CO [22]; red: biogenic mixture [6, 23]; orange: natural gas [21]; blue: CH_4.

Table 1 Overview of gas mixtures (all % in mol fraction) considered; *: calculation only. All data on ignition delay time, *present work*.

Fuel	Share ethanol / %	Ignition delay time τ		Laminar flame speed S_u		
		p/bar	φ	T/K	p/bar	*Ref.*
Experimental						
C_2H_5OH	100	1	1.0	298	1	[18]
		4	1.0	343*		
				363		
				453		
				373	1	[17]
					5	
C_2H_5OH in NG	10	1	0.5; 1.0	373*	1	*p.w.*
		4	0.5; 1.0			
Natural gas (NG)	0	1	0.5; 1.0	373	1	[21]
		4	0.5; 1.0			[6]
Calculations						
C_2H_5OH in NG	10	1	0.5; 1.0	373	1	*p.w.*
		4	0.5; 1.0		5	
	20	1	0.5; 1.0	373	1	*p.w.*
		4	0.5; 1.0		5	
	50	1	0.5; 1.0	373	1	*p.w.*
		4	0.5; 1.0		5	

GOAL AND APPROACH

In the present work, further insight into the combustion behavior of ethanol co-fired with natural gas, occurring in a micro gas turbine, in particular, shall be provided. We focus on two major combustion properties - ignition delay time and burning velocity – for temperature, pressure and fuel air regimes typical for so called "micro gas turbine combustors". Within the present work, new experiments are performed concerning ignition of mixtures of 100% ethanol [24] and of 10% share to natural gas [25] (in present work, all % are given in mol fraction). Experimental data on burning velocity are taken from an own recent investigation [6] and from literature [17-18], see Table 1. The experimental data are compared with predictions of three detailed reaction models: An in-house reaction model (DLR-RG) and two models taken from literature [20, 26]. By using the validated in-house reaction model (DLR-RG), the combustion characteristics of mixtures of ethanol, pure and in different shares to natural gas, are predicted, with respect to ignition delay times τ_{ign} and laminar flame speed S_u. Finally, these results are compared to those of natural gas.

Experimental

Within the present work, an experimental data base on the ignition behavior of mixtures of pure ethanol as well as of 10% share to natural gas is created. This also enables the validation of detailed reaction models for a better understanding of the combustion of co-firing of sustainable produced alcohols (ethanol) with natural gas.

Experimental data on ignition delay times

The experiments were performed applying the shock tube technique as an ideal tool to provide the temperature and pressure needed combined with a sensitive detection method, for radicals which are suited to serve as an indicator of ignition, *e.g.* CH* and OH*. Details about the shock tube used in the present work have been described earlier [5, 21] and thus, no further information is given in this work, for the sake of brevity. It should be noted that the estimated uncertainty in reflected shock temperature is less than ±10 K in the temperature range of our measurements resulting in an uncertainty of values of the ignition delay times of $\Delta\tau/\tau < 2$ %.

In the present work, all ignition delay times reported are due to the observation of CH* (at 431 nm) selected by narrow band pass filters (FWHM = 5 nm) and measured with a photomultiplier. All ignition delay time values are determined by measuring the time difference between the initiation of the system by the reflected shock wave and the occurrence of the CH* maximum (Fig. 2). Within the present work, ignition delay times can be measured for observation times up to 9 ms. Depending on this period, pressure and thus, temperature are considered as a function of time: $p = p(t)$, $T = T(t)$.

Fig. 2 Pressure (right axis) and emission signals (left axis) of a $C_2H_5OH/O_2/Ar$ mixture (φ = 1.0,) at p_5 = 4.12 bar and T_5 = 1050 K, dilution with Ar 1:5.

Experimental data on burning velocities

Experimental data on burning velocity were taken from our own recent investigation [6] applying the cone angle method [19] and from literature [17-18] where available, see Table 1.

Fuel mixtures measured

The ignition delay times of (i) ethanol as well as of (ii) 10% ethanol / natural gas (92% methane, 8% ethane) mixtures are determined. The fuel / oxygen / argon mixture (φ = 0.5 and 1.0, $[O_2]$ / [Ar] = 21% / 79%) is diluted with argon (20% mixture / 80% Ar, defined as dilution 1:5). The experimental conditions of the experiments performed are listed in Table 2; the compositions of the mixtures used are given in Table 3.

Table 2 Measurement of ignition delay time: Experimental conditions.

Fuel	φ	Pressure p / bar	Temperature T / K
C_2H_5OH	1.0	0.91-1.06 4.05-4.61	1094-1675 1005-1560
0%C_2H_5OH	0.5	0.91-1.17	1339-1953

in NG	0.5	4.00-4.19	1162-1705
	1.0	0.94-1.30	1281-1911
	1.0	4.06-4.37	1165-1836

Table 3 Measurement of ignition delay times: Composition (in mole fraction) of the gas mixtures used.

Fuel \ Species, in ppm	C_2H_5OH	C_2H_6	CH_4	O_2	Ar	φ
C_2H_5OH	12527	-	-	38985	948487	1.0
	12972	-	-	39163	947864	1.0
10%C_2H_5OH in NG	894	646	7402	40013	951045	0.5
	1738	1256	14389	38369	944247	1.0

Modeling

The measured data of ignition delay time as well as the data of burning velocity serve as validation data for the performance of three detailed reaction models (see below) with respect to these two major combustion properties.

The main features of the detailed reaction models used are given in Table 4. Note that reactions leading to chemiluminescence like $C_2H + O = CH^* + CO$, $CH + O_2 = CO + OH^*$, and $H + O + M = OH^* + M$ and thermal and spectroscopic de-excitation reactions of CH* and OH* [27] are added to the mechanisms for comparison with the experimentally detected chemiluminescence maxima in the post-reflected shock regime.

Two public-domain detailed reaction models are used: (i) the one of Curran *et al.* [14] developed for describing the ignition of propanol isomers (*normal* and *iso*); and (ii) the one of Marinov [26], a comprehensive mechanism for the oxidation of ethanol.

The in-house detailed reaction model used is the so called DLR-RG model used previously for modeling the ignition behavior of several fuels, with natural gas, synthetic gas, and biogenic gas among them [21, 28-29]. The DLR-RG model is based on the RAMEC model [30] 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 the one given by Li *et al.* [31], as this leads to much better predictions of ignition delay times for hydrogen systems [21].

Computer simulations of the laminar premixed flames are performed with the SANDIA code PREMIX [32], with thermal diffusion, for the assumption of a free flame. Care was taken in the computations to reach the final solution (no evolution of laminar flame speed when the number of mesh points is increased); typically more than 300 mesh points are used. The calculation of ignition-delay times is carried out using a Multiple Plug Flow Reactor (MPFR) code developed at DLR Stuttgart to take into account gas dynamic effects which cause pressure and temperature variations; for details see [5, 21]. The MPFR code which is an extension to the SANDIA code SENKIN [33] based on the CHEMKIN II package [34-35], decouples the effects of heat release from the pressure development caused by the gas dynamics of the shock tube and combines pressure relaxation effects along the shock propagation direction.

Table 4: Detailed chemical kinetic reaction models

Reference	Species	Reactions
Curran *et al.* [14]	237	1415
With n- and iso-propanol model		219
Marinov [26]	58	383
DLR-RG, *p.w.*	65	399
DLR-RG [21, 28-29]	65	359

RESULTS AND DISCUSSION

The experimental data serve as a sound base for validation of detailed reaction models, to demonstrate the influence of temperature and pressure on the burning velocity and the ignition delay. The comparison between experimental and predicted data will be presented, starting with ethanol mixtures, followed by natural gas mixtures with a share of 10% ethanol. Note that for studying the ignition behavior of the mixtures, experiments were performed in an O_2/Ar atmosphere diluted by Ar, 1:5; whereas all investigations on the burning velocity of the mixtures were done in an O_2/N_2 (air) atmosphere. At the end, the results will be compared, for a better

to the corresponding data of natural gas represented by a so-called reference gas (92 vol% CH_4 and 8 vol% C_2H_6) reflecting a typical composition of natural gas.

Ethanol mixtures

The reaction model of the present work (DLR-RG) is describing very well the ignition and the heat release of the ethanol-air mixtures studied in the present work (see Figs. 3-5).

Ignition delay

Ignition delay times of ethanol/oxygen/argon mixtures (φ = 1.0, [O_2] / [Ar] = 21 vol% / 79 vol%) were measured at a dilution of 1:5 (20 % mixture / 80 % Ar) at two pressure regimes, at about 1 bar and 4 bar, respectively, and at temperatures ranging between 1000 K to about 1660 K. Detailed information on the composition and the initial conditions were given earlier, in Tables 2 and 3.

In Fig. 3a (1 bar) and Fig. 3b (4 bar) the measured data (symbols) are compared to MPFR-CHEMKIN II [21] predictions (curves) at constant initial conditions using three detailed reaction models mentioned earlier (see Table 4). The predictions using the mechanism of the present work (full line) result in an excellent representation of the experimental data, in particular for lower temperatures and for higher pressures.

Burning velocity

In Figs. 4-5, the comparison between measured (symbols) and predicted (curves) values of the burning velocity of ethanol/air mixtures is given: (i) for several preheat temperatures T_0 at p = 1 bar (Fig. 4); and (ii) for two pressures (p = 1 bar and p = 5 bar) at a constant preheat temperature (T_0 = 373 K, Fig. 5). Values of the laminar flame speed were obtained over a fuel equivalence ratio φ, within about $0.6 < \varphi < 1.8$. Note that experimental data were gathered from literature [17-18].

The reaction model of the present work (DLR-RG) succeeds in predicting not only the main features (shape, trend) but also the exact position of the maximum burning velocity S_u when compared to the experimental data. This is true for the measurement of the burning velocity in a counterflow configuration a method considered often as the most reliable one for determining values of laminar flame speeds, at ambient pressure and for several different preheat temperatures (Fig. 4). When comparing the predictions obtained using the present reaction model to the experimental data performed recently within a collaborative study applying several different methods for determining burning velocity [18] both at atmospheric and at elevated pressure (Fig. 5), the reaction model succeeds in predicting shape, trend and exact position of the measured burning velocities. The experimental data are matched by the model's results at elevated pressure, whereas for ambient pressure the experimental data which are lower compared to the ones of Egolfopoulos *et al.* [18] are overpredicted near stoichiometric fuel air ratios, by about 15%.

Natural gas/ethanol mixtures

The reaction model of the present work (DLR-RG) is describing very well the ignition (see Figs. 6-8) of the 10%- ethanol-air mixtures studied in the present work. Predictions by this reaction model for the laminar flame speed of 10%-ethanol-air mixtures are plotted in Fig. 9.

Ignition delay times

Ignition delay times of fuel/oxygen/argon mixtures with the fuel consisting of 10% ethanol added to natural gas represented by a mixture of 92% methane and 8% ethane were experimentally investigated, at a dilution of 1:5 with argon. Ignition delay times were determined for a fuel lean and a stoichiometric mixture, at two pressures, p = 1 bar and p = 4 bar, respectively, and at temperatures ranging between 1250 K up to about 1900 K.

The modeling calculations done with the reaction models of Curran *et al.* [14] and the one of the present work, DLR-RG, result in a good comparison with the measured data (Figs. 6-7). The mechanism of Marinov leads to an overprediction of nearly all experimentally derived ignition delay time data, within the whole temperature and

pressure range considered. From Fig. 8 it is clearly to be seen that the reaction model of the present work, DLR-RG, is matching the measured ignition delay time data best, within the entire parameter range.

Fig. 3 Comparison between measured (symbols) and calculated (curves) ignition delay times of ethanol/O_2/Ar mixtures (φ = 1.0, dilution with Ar 1:5). Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov [26], dashed, blue; Curran *et* al. [14], dotted, red. Left: p = 1 bar; Right: p = 4 bar.

Fig. 4 Burning velocities of ethanol/air mixtures at p = 1 bar and four preheat temperatures: T_0 = 298 K, T_0 = 343 K, T_0 = 363 K, and T_0 = 453 K. Measurements (symbols): triangles: Egolfopoulos *et al.* [18]. Calculations (curves, small symbols) with DLR-RG.

Fig. 5 Burning velocities of ethanol/air mixtures at T_0 = 373 K for p = 1bar (open symbols) and p = 5 bar (full symbols). Measurements: Beeckmann *et al.* [17]; calculations (curves, small symbols) with DLR-RG.

Fig. 6 Comparison between measured (symbols) and calculated (curves) ignition delay times of 10%ethanol/natural gas/O_2/Ar mixtures (φ = 0.5, dilution with Ar 1:5). Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov *et al.* [26], dashed, blue; Curran *et al.* [14], dotted, red. Left: p = 1 bar; Right: p = 4 bar.

Fig. 7 Comparison between measured (symbols) and calculated (curves) ignition delay times of 10%ethanol/natural gas/O_2/Ar mixtures (φ = 1.0, dilution with Ar 1:5). Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov [26], dashed, blue; Curran *et al.* [14], dotted, red. Left: p = 1 bar; Right: p = 4 bar.

Fig. 8 Comparison between measured (symbols) and calculated (curves) ignition delay times of 10 %-ethanol/natural gas/O_2/Ar mixtures (dilution with Ar 1:5) for p = 1 bar and p = 4 bar. Calculations with reaction

models of: DLR-RG, *p.w.*, full, black; Marinov [26], dashed, blue; Curran *et al.* [14], dotted, red. Left: $\varphi = 0.5$; Right: $\varphi = 1.0$.

Burning velocity

No experimental data exist for burning velocities of 10%-ethanol/natural gas/air mixtures. Therefore, calculations were done using the reaction model DLR-RG. Results show that this mechanism is able to describe the ignition behavior of ethanol and ethanol/natural gas/air mixtures as well as the burning velocities of ethanol/air mixtures within the parameter range considered. Results are plotted in Fig. 9, also for pure ethanol/air mixtures. The predicted laminar flame speed of 10%-ethanol/natural gas /air mixtures (green stars) are about 25% lower than those for pure ethanol, at the position of the maximum flame speed, for ambient and elevated pressure.

Comparison with results on natural gas mixtures

The results obtained earlier for the two different kinds of fuel - pure ethanol and 10% share of ethanol in natural gas - investigated focusing on their ignition and heat release characteristics are compared with those of natural gas, a fuel that is typically burned in stationary large-scale gas turbines. Also, calculations are performed for a variable share of ethanol in natural gas ranging between 0 (equal to natural gas) and 100 % (equal to pure ethanol), for an insight into the spread and range of the characteristic combustion properties considered, as a function of pressure, temperature, and fuel-air ratio; see Figs. 11-12 for ignition delay times and Fig. 14 for laminar flame speeds, respectively.

It is interesting to note that compared to natural gas, ethanol shows an enhanced reactivity with respect to ignition delay times, but not with respect to laminar flame speeds. This is mainly due to the fact that the rate of ignition is mostly influenced by the availability of a radical pool (H, OH, O radicals) which itself is determined of the temperature dependent rate coefficients of radical forming as well as chain branching reactions. In addition,

ignition is studied at a constant temperature, whereas investigating burning velocities implies combustion in a flame occurring within a temperature range, from preheat temperature up to adiabatic flame temperature. Here, reactions with CO and HCO species involved are among the most important ones due to their high reaction enthalpy [6].

Fig. 9 Comparison between calculated (curve, small symbol, DLR-RG model, *p.w.*) and measured (large symbol, Beekmann *et al.* [17]) burning velocities of ethanol/air and 10%ethanol/natural gas/air mixtures at T_0 = 373 K for p = 1 bar (open symbol) and p = 5 bar (full symbol).

Ignition delay times

Ignition delay times of pure ethanol/oxygen/argon mixtures (φ = 1.0, [O_2] / [Ar] = 21% / 79%) are about a factor of ten lower than those of natural gas, for ambient and elevated pressure (4 bar) which is typical for combustion occurring in a micro gas turbine (refer to Fig. 10). Note that the predictions using the reaction model DLR-RG results in an excellent match of the measured data. Therefore, further predictions were done, for a variable share of ethanol in natural gas, for the parameter range typical to combustion in a micro gas turbine which has a large potential with respect to fuel flexibility with alternative fuels such as ethanol; see Fig. 11 (stoichiometric) and Fig. 12 (fuel lean). Ignition delay times for natural gas mixtures with a share of 10 and 20 % ethanol, respectively, are predicted considerably shorter than the ones of pure natural gas mixtures, up to a factor of 4.

Burning velocity

Laminar flame speeds of fuel/air mixture, with pure ethanol as well as with a 10%-amount of ethanol in natural gas, are plotted together with those of natural gas, again, for ambient (p = 1 bar) and elevated pressure (p = 5 bar), see Fig. 13. All data - experimental and calculated – are given for the preheat temperature T_0 = 373 K. Pure ethanol/air mixtures have higher burning velocities than natural gas/air mixtures, by about 25% at ambient pressure and up to about 45% at higher pressure (p = 5 bar), at φ = 1.15 close to the position of the highest laminar flame speed. Note that the reaction model predicts measured burning velocities of methane (Fig. 1a); furthermore, burning

velocities predicted for natural gas (92% CH_4 and 8% C_2H_6) are very similar to the one of methane (Fig. 1a). Again, the DLR-RG reaction model is used to predict laminar flame speeds of fuel/air mixtures with a variable share of ethanol in natural gas, for ambient and elevated pressures (see Fig. 14).

CONCLUSIONS

Biomass is a clean, renewable energy source with a large potential to contribute significantly to future production of electricity, in both centralized and decentralized units. Among the different concepts, the use of a fuel flexible micro gas turbine, but also the coupling of a gasifier or a biogas reactor with a fuel cell and a micro gas turbine following the idea of a hybrid plant was discussed [11] in order to further increase the electrical efficiency, also for small scale power generation.

In the present work, two major combustion properties of ethanol, having a high potential to serve as a fuel for a more sustainable power generation, were studied by the combination of experiments and chemical kinetic modeling. Parameters such as temperature, pressure, and fuel-air ratio were selected to correspond to the typical operating range of micro gas turbines.

The ignition delay times of pure ethanol/oxygen/argon mixtures are more than one order of magnitude shorter than those of natural gas/oxygen/argon mixtures, at ambient and elevated (p = 4 bar) pressures, depending on temperature. For mixtures with a relatively low amount of ethanol (10%), the ignition delay times differ by a factor of 2 at higher temperatures; at lower temperatures, the ignition delay times data of 10% ethanol/oxygen/argon mixtures are about a factor of 4 shorter than those of pure natural gas mixtures.

The predicted laminar flame speed data of pure ethanol/air mixtures are significantly higher compared to those of natural gas/air mixtures, by up to 25% at ambient pressure, and up to 45% at elevated pressure (p = 5 bar). Mixtures with a significant amount of ethanol in natural gas have higher laminar flame speed data, by about 5% for a

10% share of ethanol, and by about 10% for a 20% share of ethanol, respectively, compared to natural gas/air mixtures.

Ignition delay times and laminar flame speeds were investigated also by modeling calculations with detailed chemical kinetic reaction models. The in-house reaction model, DLR-RG, was describing the experimental data base excellent, within the entire parameter range and for the fuels considered: pure ethanol, natural gas, and fuels with a variable amount of ethanol in natural gas.

Thus, the present work is contributing to a better and a more sophisticated design of a burner or the combustion chamber by enabling CFD calculations with a reliable and validated reaction model once the detailed reaction model has been further reduced, with respect to the number of species and reactions incorporated.

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Fig. 10 Comparison between measured (symbols) and calculated (curves) ignition delay times of fuel/O_2/Ar mixtures (φ = 1.0, dilution with Ar 1:5): triangles: ethanol; circles: natural gas + 10% ethanol; squares: natural gas. Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov [26], dashed, blue; Curran *et al.* [14], dotted, red. Left: p = 1 bar; Right: p = 4 bar.

Fig. 11 Predicted (curves) ignition delay times of fuel/O_2/Ar mixtures (φ = 1.0, dilution with Ar 1:5): ethanol: black, full; natural gas +10% ethanol: dashed, red; natural gas + 20% ethanol: dotted, orange; natural gas +50% ethanol: green, dashed-dotted; natural gas: blue, dashed-dotted-dotted. Calculations with reaction model of DLR-RG, *p.w.*. Left: p = 1 bar; Right: p = 4 bar.

Fig. 12 Predicted (curves) ignition delay times of fuel/O_2/Ar mixtures (φ = 0.5, dilution with Ar 1:5): ethanol: black, full; natural gas +10% ethanol: dashed, red; natural gas + 20% ethanol: dotted, orange; natural gas +50% ethanol: green, dashed-dotted; natural gas: blue, dashed-dotted-dotted. Calculations with reaction model of DLR-RG, *p.w.*. Left: p = 1 bar; Right: p = 4 bar.

Fig. 13 Comparison between calculated (curves) and measured (large symbols, Beekmann *et al*. [17]) burning velocities of fuel/air mixtures at T_0 = 373 K: natural gas: (black); ethanol: (green); natural gas + 10% ethanol: (red). Calculations with reaction model DLR-RG, *p.w.*. Left: p = 1 bar; Right: p = 5 bar.

Fig. 14 Comparison between calculated (curves) and measured (large symbols, Beekmann *et al*. [17]) burning velocities of fuel/air mixtures at T_0 = 373 K: triangles: ethanol; circles: 90% natural gas + 10% ethanol; 80% natural gas + 20% ethanol; 50% natural gas + 50% ethanol; squares: natural gas. Calculations with reaction model DLR-RG, *p.w.*. Left: p = 1 bar; Right: p = 5 bar.

Nomenclature

p = pressure

t = time

T = temperature

S_u laminar flame speed

Greek Symbols

φ = equivalence ratio

τ = ignition delay time

ρ = density

Subscripts

0 = initial

ign = ignition

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Table 1 Overview of gas mixtures (all % in mol fraction) considered; *: Calculation only. All data on ignition delay time, *present work*.

Fuel	Share ethanol / %	Ignition delay time τ		Laminar flame speed S_u		
		p/bar	φ	T/K	p/bar	*Ref.*
Experimental						
C_2H_5OH	100	1 4	1.0 1.0	298 343* 363 453	1	[18]
				373	1 5	[17]
C_2H_5OH in NG	10	1 4	0.5; 1.0 0.5; 1.0	373*	1	*p.w.*
Natural gas (NG)	0	1 4	0.5; 1.0 0.5; 1.0	373	1	[21] [6]
Calculations						
C_2H_5OH in NG	10	1 4	0.5; 1.0 0.5; 1.0	373	1 5	*p.w.*
	20	1 4	0.5; 1.0 0.5; 1.0	373	1 5	*p.w.*
	50	1 4	0.5; 1.0 0.5; 1.0	373	1 5	*p.w.*

Table 2 Measurement of ignition delay time: Experimental conditions.

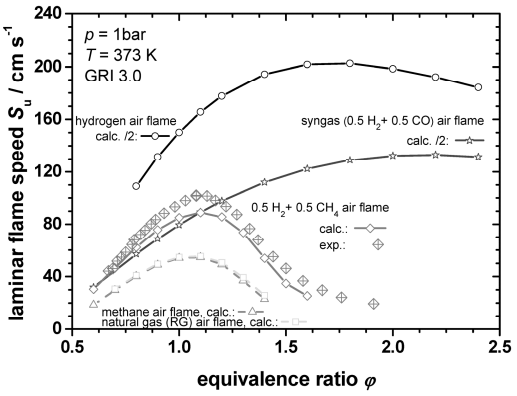
Fuel	φ	Pressure p / bar	Temperature T / K
C_2H_5OH	1.0	0.91-1.06	1094-1675
		4.05-4.61	1005-1560
0%C_2H_5OH in NG	0.5	0.91-1.17	1339-1953
	0.5	4.00-4.19	1162-1705
	1.0	0.94-1.30	1281-1911
	1.0	4.06-4.37	1165-1836

Table 3 Measurement of ignition delay times: Composition (in mole fraction) of the gas mixtures used.

Species, in ppm / Fuel	C_2H_5OH	C_2H_6	CH_4	O_2	Ar	φ
C_2H_5OH	12527	-	-	38985	948487	1.0
	12972	-	-	39163	947864	1.0
10%C_2H_5OH in NG	894	646	7402	40013	951045	0.5
	1738	1256	14389	38369	944247	1.0

Table 4 Detailed chemical kinetic reaction models.

Reference	Species	Reactions
Curran *et al.* [14]	237	1415
With n- and iso-propanol model		219
Marinov [26]	58	383
DLR-RG, *p.w.*	65	399
DLR-RG [21, 28-29]	65	359



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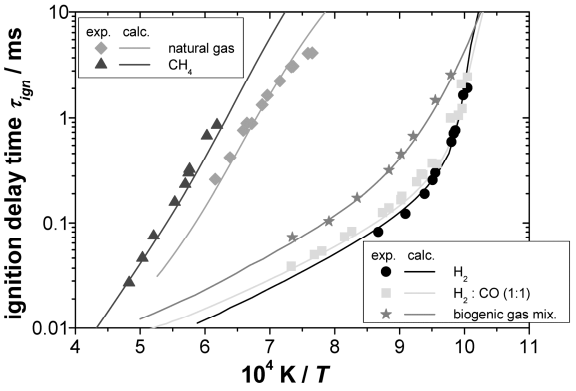

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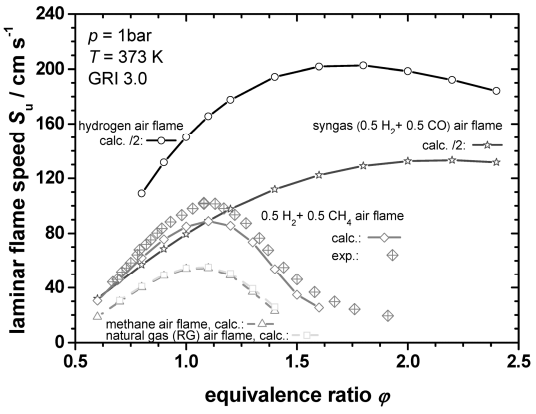
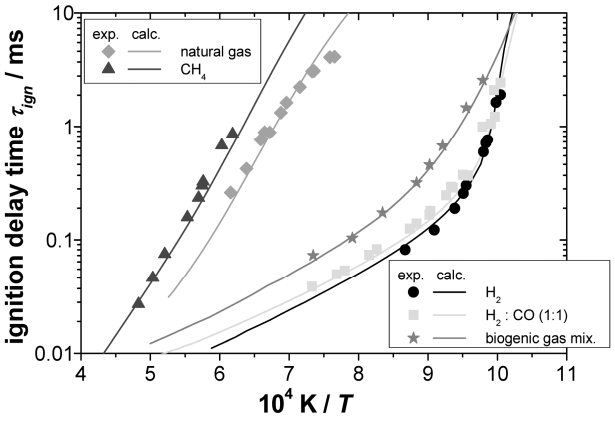
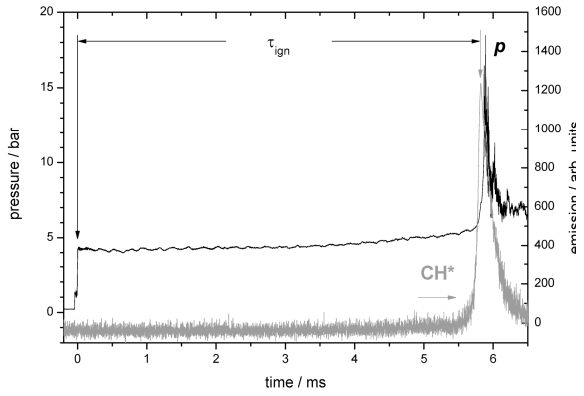
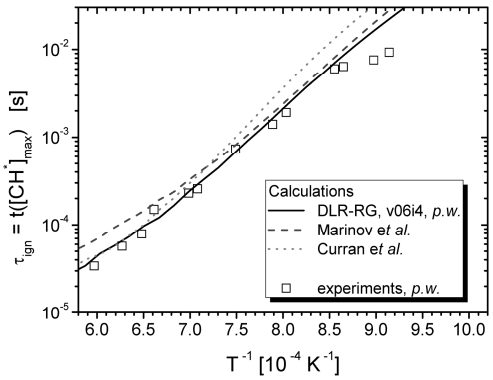




Characteristic combustion properties. Left: Laminar flame speeds of different fuel-air mixtures, p = 1 bar, T_0 = 373 K. Experiments – 50%H_2/50% methane mixture [8]; calculations (curves) with a detailed reaction model, GRI 3.0 [20]. Right: Ignition delay times of different fuel-air mixtures diluted in argon 1:5. Comparison between experiment (symbols) and calculations (curves, with DLR-RG reaction model, *p.w*) for: φ = 1.0, p = 4 bar, oxidizer: 79% Ar, 21% O_2. Black: H_2 [21]; green: 50% H_2/ 50% CO [22]; red: biogenic mixture [6, 23]; orange: natural gas [21]; blue: CH_4.



Pressure (right axis) and emission signals (left axis) of a $C_2H_5OH/O_2/Ar$ mixture (φ = 1.0,) at p_5 = 4.12 bar and T_5 = 1050 K, dilution with Ar 1:5.



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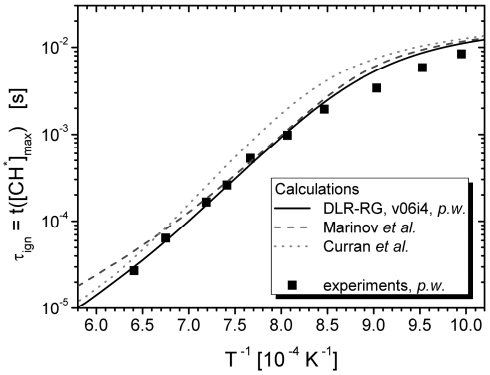

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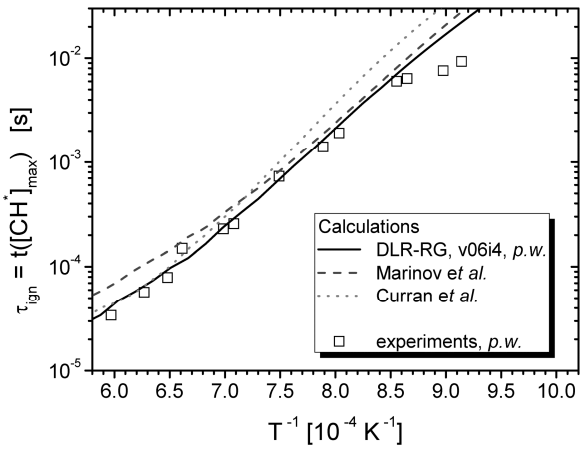
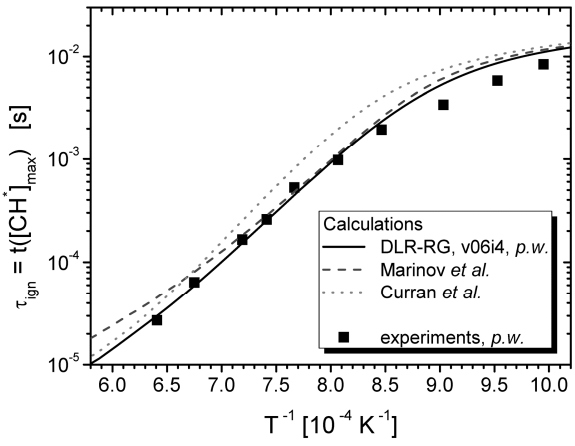
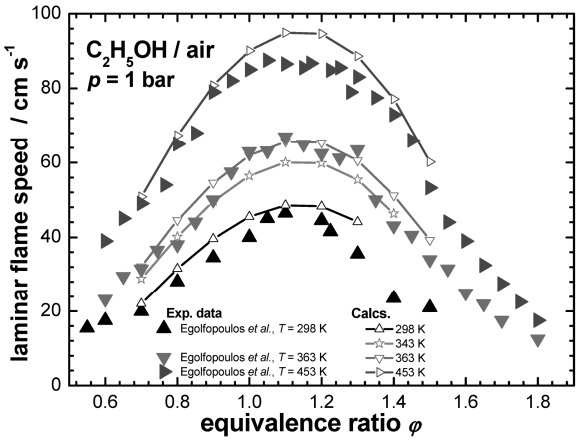
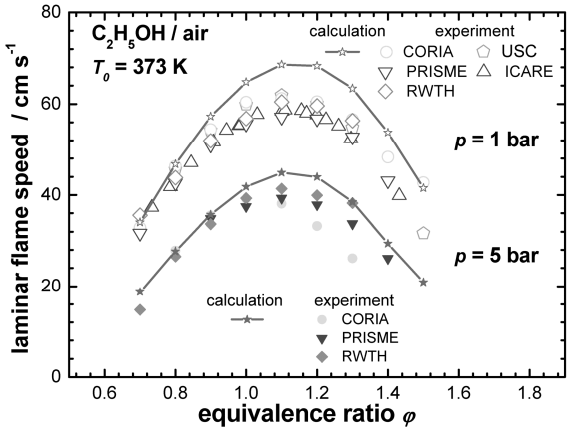




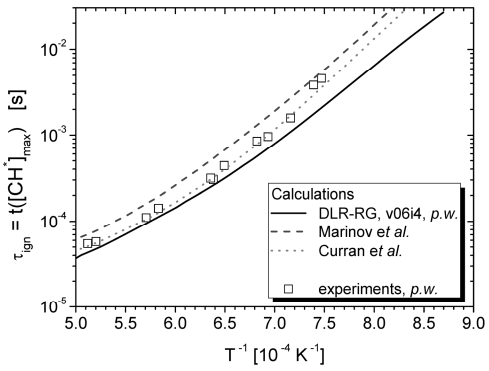
Comparison between measured (symbols) and calculated (curves) ignition delay times of ethanol/O_2/Ar mixtures (φ = 1.0, dilution with Ar 1:5). Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov [26], dashed, blue; Curran *et* al. [14], dotted, red. Left: p = 1 bar; Right: p = 4 bar.



Burning velocities of ethanol/air mixtures at p = 1 bar and four preheat temperatures: T_0 = 298 K, T_0 = 343 K, T_0 = 363 K, and T_0 = 453 K. Measurements (symbols): triangles: Egolfopoulos *et al.* [18]. Calculations (curves, small symbols) with DLR-RG.



Burning velocities of ethanol/air mixtures at $T_0 = 373$ K for $p = 1$bar (open symbols) and $p = 5$ bar (full symbols). Measurements: Beeckmann *et al.* [17]; calculations (curves, small symbols) with DLR-RG.



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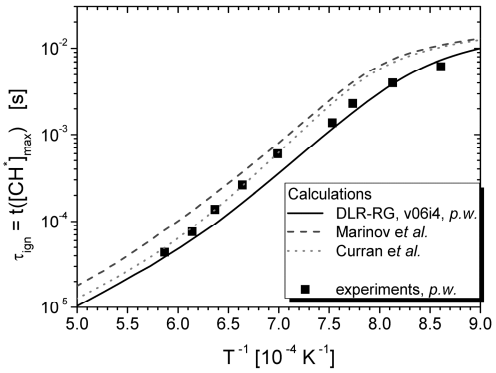

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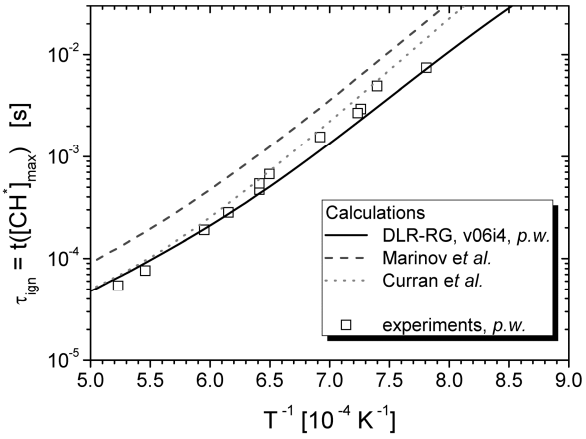
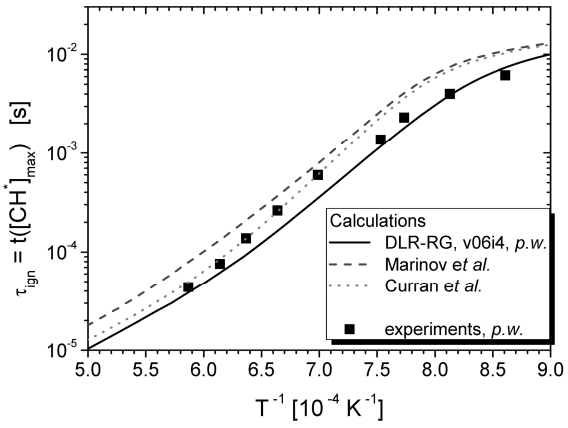
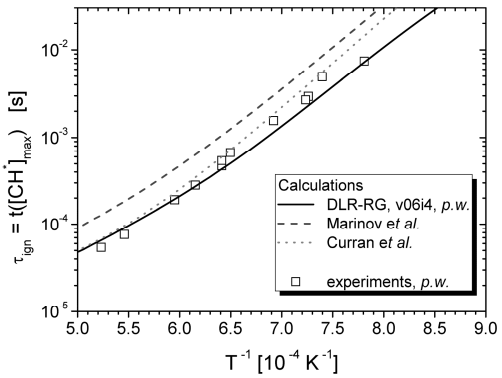




Comparison between measured (symbols) and calculated (curves) ignition delay times of 10%ethanol/natural gas/O2/Ar mixtures (φ = 0.5, dilution with Ar 1:5). Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov et al. [26], dashed, blue; Curran *et al.* [14], dotted, red. Left: p = 1 bar; Right: p = 4 bar.



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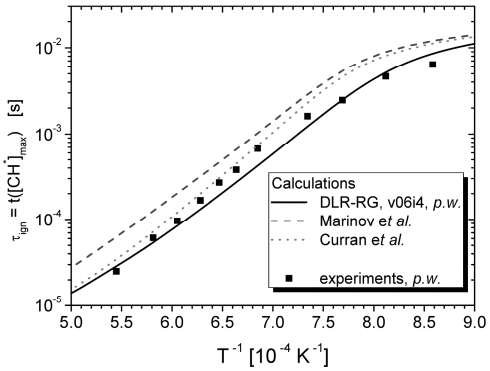

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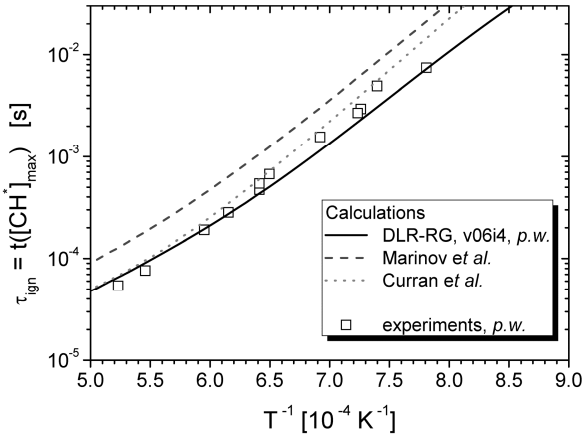
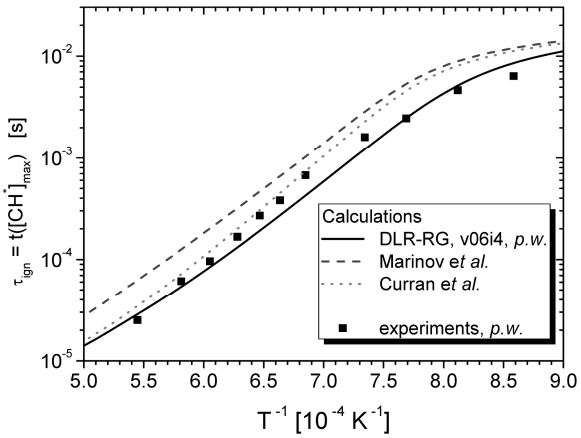
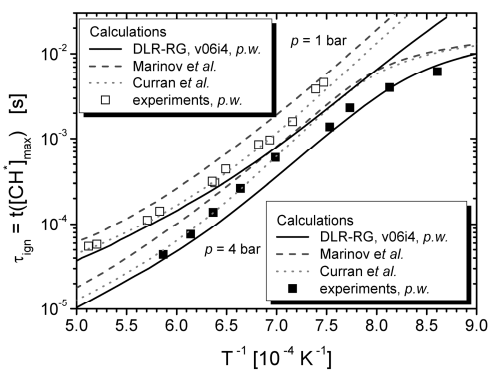




Comparison between measured (symbols) and calculated (curves) ignition delay times of 10%ethanol/natural gas/O_2/Ar mixtures (φ = 1.0, dilution with Ar 1:5). Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov [26], dashed, blue; Curran *et al.* [14], dotted, red. Left: p = 1 bar; Right: p = 4 bar.



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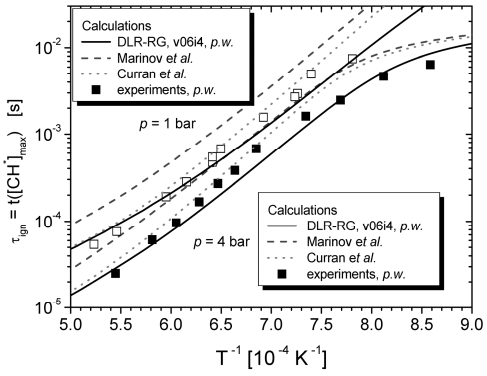

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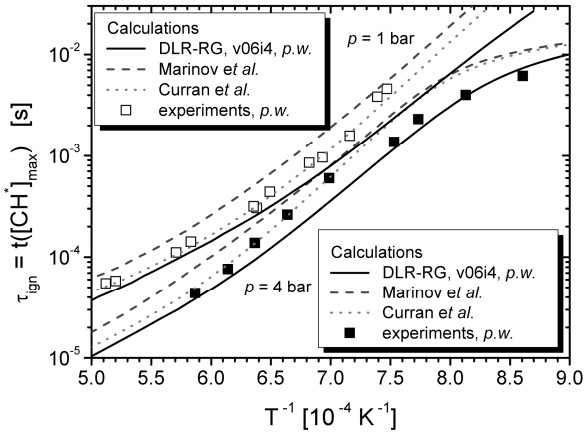
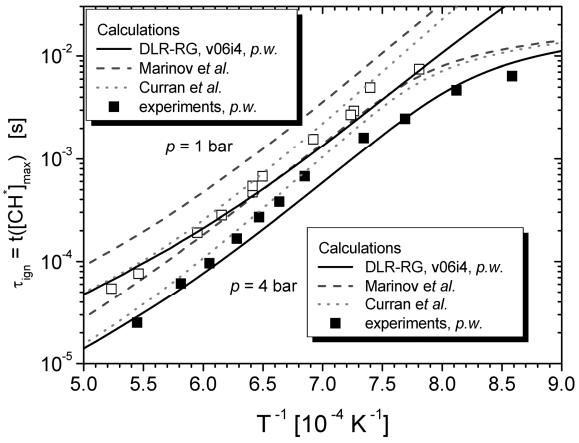
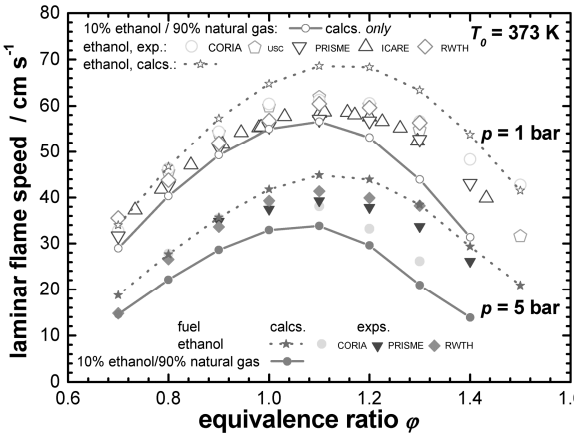
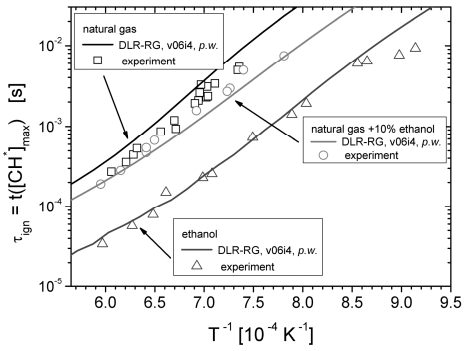




Comparison between measured (symbols) and calculated (curves) ignition delay times of 10 %-ethanol/natural gas/O_2/Ar mixtures (dilution with Ar 1:5) for p = 1 bar and p = 4 bar. Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov [26], dashed, blue; Curran *et al.* [14], dotted, red. Left: $\varphi = 0.5$; Right: $\varphi = 1.0$.



Comparison between calculated (curve, small symbol, DLR-RG model, *p.w.*) and measured (large symbol, Beekmann *et al.* [17]) burning velocities of ethanol/air and 10%ethanol/natural gas/air mixtures at T_0 = 373 K for p = 1 bar (open symbol) and p = 5 bar (full symbol).



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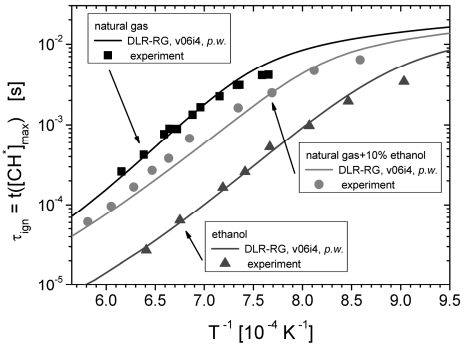

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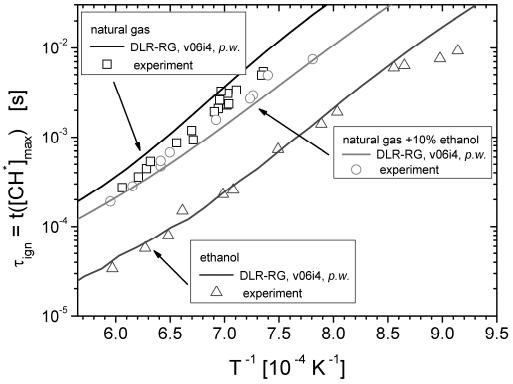
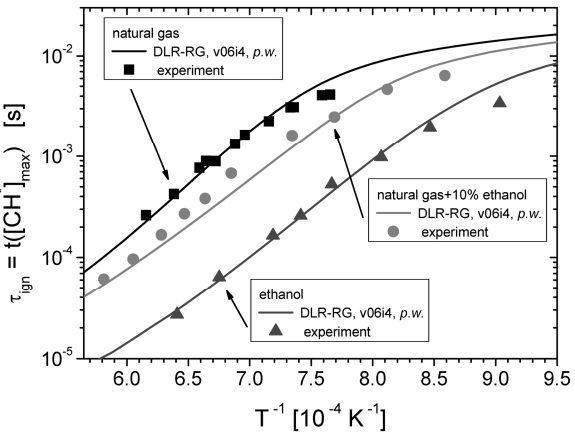
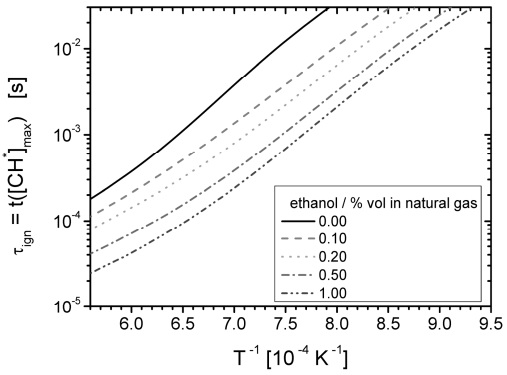




Comparison between measured (symbols) and calculated (curves) ignition delay times of fuel/O_2/Ar mixtures (φ = 1.0, dilution with Ar 1:5): triangles: ethanol; circles: natural gas + 10% ethanol; squares: natural gas. Calculations with reaction models of: DLR-RG, *p.w.*, full, black; Marinov [26], dashed, blue; Curran *et al.* [14], dotted, red. Left: p = 1 bar; Right: p = 4 bar.



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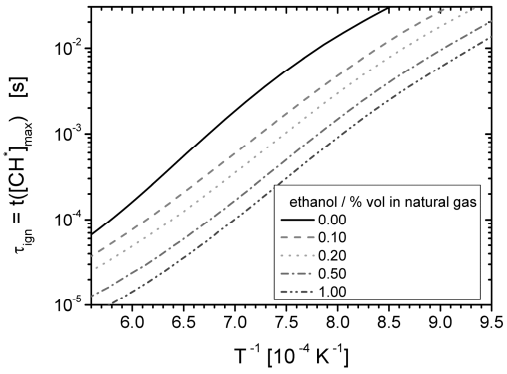
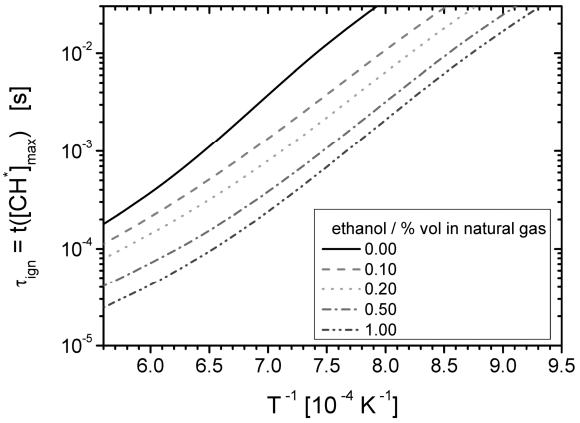
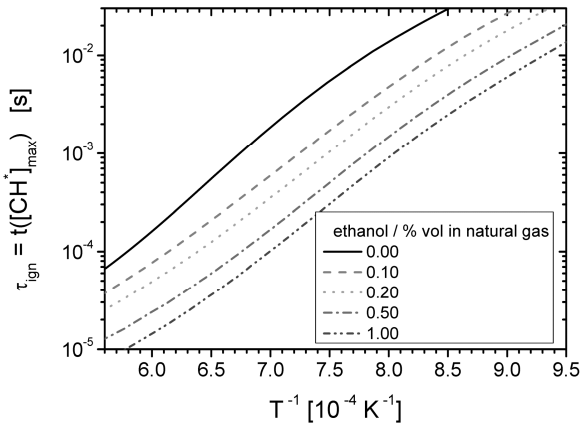


Fig11_right.tif





Predicted (curves) ignition delay times of fuel/O_2/Ar mixtures (φ = 1.0, dilution with Ar 1:5): ethanol: black, full; natural gas +10% ethanol: dashed, red; natural gas + 20% ethanol: dotted, orange; natural gas +50% ethanol: green, dashed-dotted; natural gas: blue, dashed-dotted-dotted. Calculations with reaction model of DLR-RG, *p.w.*. Left: p = 1 bar; Right: p = 4 bar.

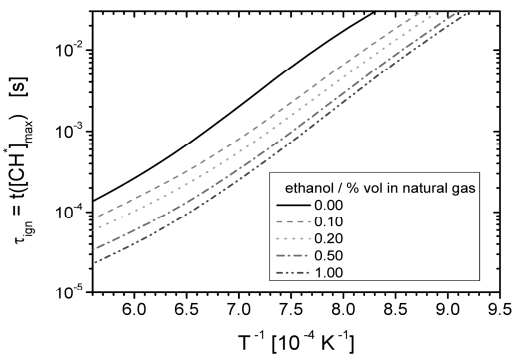


Fig12_left.tif

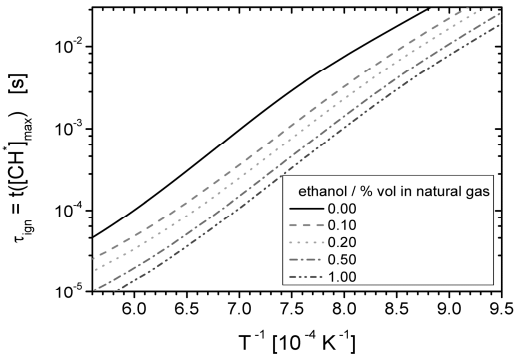
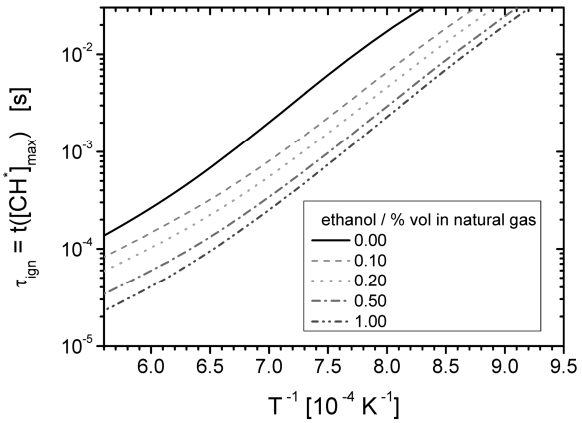
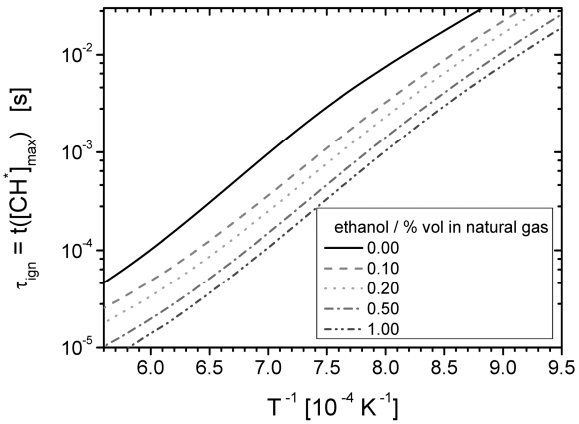


Fig12_right.tif





Predicted (curves) ignition delay times of fuel/O_2/Ar mixtures (φ = 0.5, dilution with Ar 1:5): ethanol: black, full; natural gas +10% ethanol: dashed, red; natural gas + 20% ethanol: dotted, orange; natural gas +50% ethanol: green, dashed-dotted; natural gas: blue, dashed-dotted-dotted. Calculations with reaction model of DLR-RG, *p.w.*. Left: p = 1 bar; Right: p = 4 bar.

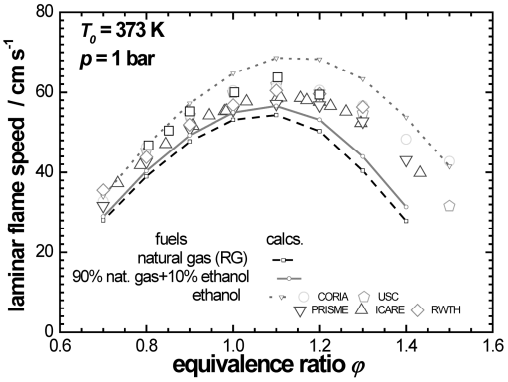


Fig13_left.tif

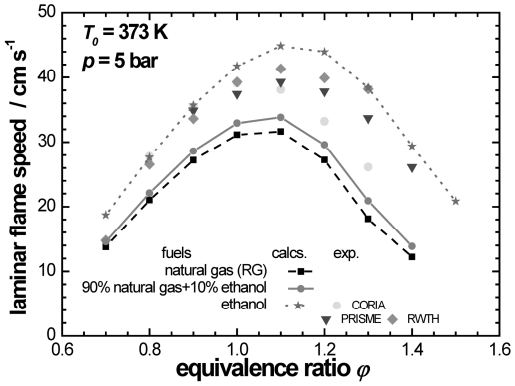
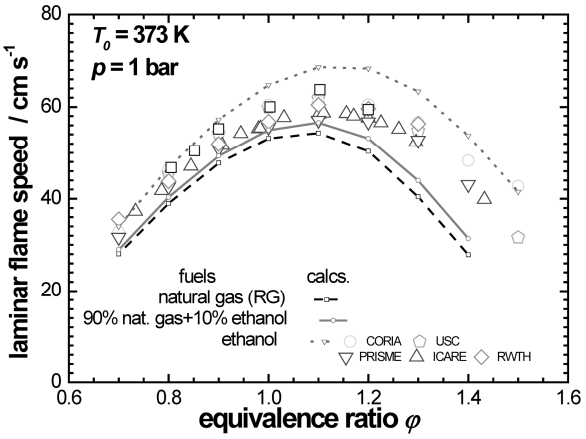
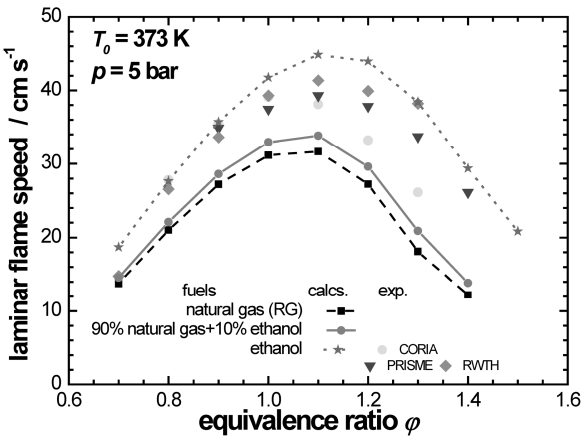
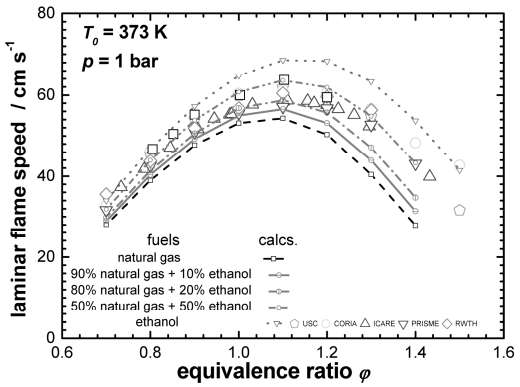


Fig13_right.t





Comparison between calculated (curves) and measured (large symbols, Beekmann *et al*. [17]) burning velocities of fuel/air mixtures at T_0 = 373 K: natural gas: (black); ethanol: (green); natural gas + 10% ethanol: (red). Calculations with reaction model DLR-RG, *p.w.*. Left: p = 1 bar; Right: p = 5 bar.



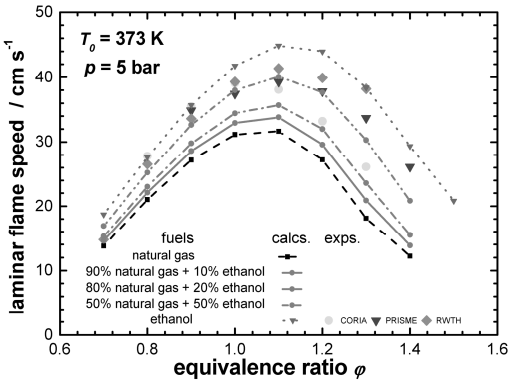
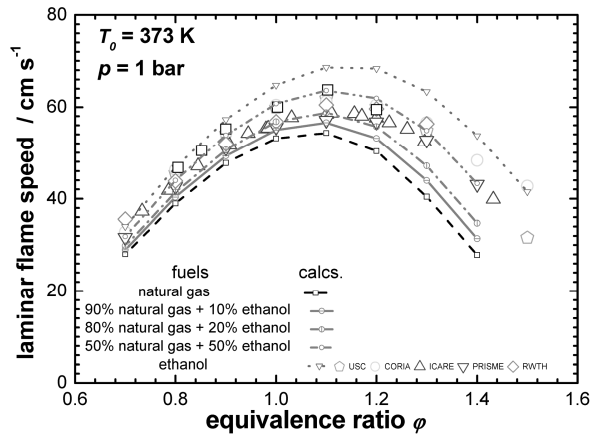
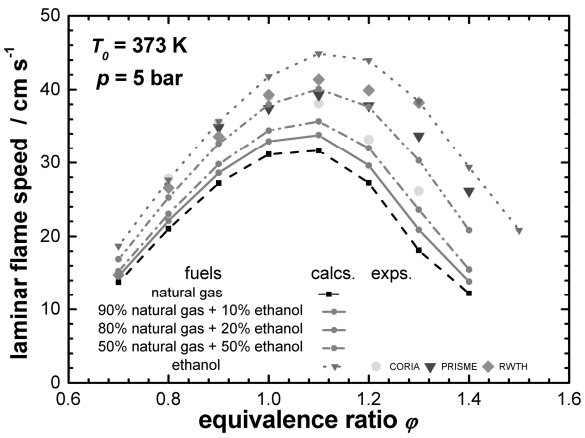


Fig14_left.tif

Fig14_right.t





Comparison between calculated (curves) and measured (large symbols, Beekmann *et al*. [17]) burning velocities of fuel/air mixtures at T_0 = 373 K: triangles: ethanol; circles: 90% natural gas + 10% ethanol; 80% natural gas + 20% ethanol; 50% natural gas + 50% ethanol; squares: natural gas. Calculations with reaction model DLR-RG, *p.w.*. Left: p = 1 bar; Right: p = 5 bar.