The Pyrolysis of Ethanol: Kinetic Modeling of Shock Tube Experiments

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Abstract
Improvements in fuel flexibility are a prerequisite, to meet the challenge of a more sustainable production of energy in the near future. To address fuel flexibility, a wide range of different fuels are considered, with alcohols among them, in particular ethanol. Therefore, in the present work, a modeling study was done by investigating the performance of three detailed chemical kinetic reaction models with respect to species profiles, in order to contribute to a better understanding of the combustion of ethanol, for a wide range of application. The experiments were performed in a single pulse shock tube, at temperatures between 1100-1500 K and at pressures of about 1 and 4 bar. Time-of-flight mass spectrometry was used as detection technique, and concentration-time profiles of the following five species were simultaneously recorded: ethanol, (ethane + ethylene + acetylene), acetaldehyde, methane, and water. An in-house reaction mechanism used earlier for describing essential combustion properties of small hydrocarbons and, in addition, two detailed reaction mechanisms gathered from literature were employed to model the measured concentration-time profiles. The overall performance as well as the predictive capabilities of the different mechanisms are discussed, also by referring to the results of sensitivity and reaction flux analysis.

Introduction

Over the last years, alternative and renewable energy resources have become increasingly important, because they contribute to the reduction of fossil hydrocarbon consumption and the corresponding emissions of carbon dioxide. In particular, alcohols are considered as promising alternative fuels or fuel additives [1].

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. Currently, ethanol plays a major role in automotive transport, but it may also serve as replacement of aviation gasoline (avgas) in small aircrafts [2]. Quite recently, producing renewable synthetic jet fuels from sugar known as alcohol to jet (ATJ) and sugar to jet (STJ) became possible [2, 3]. Also, 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 [4, 5] Besides their potential of a CO_2-neutral energy source, such facilities exhibit lower emission levels of polyaromatic hydrocarbons (PAH) and soot [6].

To optimize combustion engines for the use of ethanol as a fuel, a detailed understanding of the chemical mechanism of ignition and combustion of ethanol is essential. An indispensable tool to analyze and interpret observed fundamental combustion phenomena is chemical modeling. Previously published model mechanisms for ethanol oxidation were mainly validated in terms of measured flame speeds and ignition delay times. An additional, under chemical aspects more rigorous test is certainly the modeling of measured concentration-time profiles of one or better several simultaneously recorded species.

In this work, we report on the modeling results from a single pulse shock tube study of the pyrolysis of ethanol. Concentration-time profiles of ethanol and several stable reaction products were simultaneously recorded with time-of-flight mass spectrometry as detection technique [7].

Goal and Approach

A combined experimental and modeling approach is done, in order to provide further insight into the combustion behavior of ethanol. The predictability of the in-house detailed chemical kinetic reaction model [5] will be enhanced by adding species profiles to the set of validation experiments, besides laminar flame speeds and ignition delay times the reaction model was constructed and tested over the last years [5, 8, 9]. The ultimate goal is to contribute to reaction models validated by using a comprehensive experimental data base and within a large parameter range. Such validated chemical kinetic reaction models are needed as a prerequisite to models used in computational fluid dynamics (CFD) simulations for *e.g.* a more efficient burner and combustor design process.

In the present work, we focus on concentration-time profiles measured at ambient and elevated pressures, for temperatures mainly between 1300 and 1500 K: Ethanol (C_2H_5OH), water (H_2O) and methane (CH_4) as major products, besides acetaldehyde (CH_3CHO) and sum of ethane, ethylene, acetylene (C_2H_n).

The experimental data are compared with predictions of three detailed reaction models: An in-house reaction model (DLR-RG) [5] and two models taken from literature [10, 11].

Experimental

The experiments were performed in a shock tube behind reflected shock waves in the temperature range 1100–1500 K at pressures of about 1 and 4 bar with time-of-flight mass spectrometry (TOF-MS) as detection technique [7]. The TOF-MS was operated with electron-impact ionization at a repetition rate of 125 kHz, which corresponds to a time resolution of 8 μs. The coupling to the shock tube was accomplished in the way introduced by Kistiakowski and Bradley [12]. The shock tube itself and the method of its operation are described in more detail elsewhere [7, 13, 14].

In the experiments, different initial mole fractions of ethanol (1 or 1.5 % in neon) were used. Concentration-time profiles of C_2H_5OH (m/z 46), C_2H_n (m/z 26, with possible contributions from C_2H_2, C_2H_4, and C_2H_6), C_2H_4O (m/z 44), CH_4 (m/z 16), and H_2O (m/z 18) were simultaneously recorded. Absolute concentrations were obtained from calibration measurements with the pure substances. Table 1 summarizes the experiments and their initial conditions presented in this study.

Tab. 1: Initial conditions of the ethanol decomposition of the selected experiments [7].

	Exp. 1	Exp. 2	Exp. 3
T_0 / K	1320	1380	1400
p_0 / bar	1.2	1.1	3.6
$[C_2H_5OH]_0$ / mol cm^{-3}	1.1e-7	1.4e-7	4.7e-7
$[Ne]_0$ / mol cm^{-3}	1.0e-5	9.3e-6	3.1e-5
$[Kr]_0$ / mol cm^{-3}	1.1e-7	9.5e-8	3.7e-7

Modeling

The measured concentration-time profiles of five species including reactant and major products serve as validation data for the performance of three detailed reaction models.

The main features of the detailed reaction models used are given in Tab. 2. The in-house reaction mechanism called DLR-RG [5] has been developed over the years, in particular for describing essential combustion properties - laminar flame speeds and ignition delay times - of many fuel-air mixtures with natural gas, syngas, biogenic gases as well as ethanol and ethanol-natural gas mixtures among them [4, 5, 8, 9] over a wide range of parameters - temperature, pressure, and fuel air regimes typical for gas turbine combustors. Note that the ethanol sub-model included was taken from the work of Marinov [10].

Furthermore, two detailed ethanol models were taken from literature [10, 11] and tested in terms of their performance to reproduce the measured species profiles: from Marinov [10], and from Ranzi et al. [11].

The computer simulations were performed with the commercial software Chemical Workbench by Kintech Lab [15]. The species profiles were calculated using the calorimetric reactor model (plug flow) under adiabatic and constant pressure conditions.

Tab. 2: Detailed chemical kinetic reaction models.

Reaction Model	Species	Reactions
In-house:		
DLR-RG [5]	65	359
From literature:		
Marinov [10]	84	1699
Ranzi et al. [11]	57	383

Results and Discussion

The comparison between measured and calculated concentration profiles of five species is presented (Figs. 1-3). Also, for a better insight into the combustion of the fuel-air mixtures studied, the reaction models were analyzed by the use of sensitivity and rate of production analysis (Figs. 4-5).

In summary, the predicted species profiles are in good agreement with the measured data, with the exception of the model by Ranzi et al. [11], for which the prediction of ethanol decay tends to be too slow.

Experiments performed at ambient pressure

The ethanol decomposition and, hence, the methane build up are underpredicted by all models, in particular for the lower temperatures studied, e.g. at $T = 1320$ K (Fig. 1). Furthermore, the maximum concentration of acetaldehyde is slightly underpredicted by the investigated models. A good agreement for the species profiles of water and C_2H_n (ethane + ethylene + acetylene) is seen.

In comparison, simulations predict experimental ethanol decomposition and methane build up much better at higher temperatures ($T = 1380$ K), Figs. 2-3.

The decomposition of ethanol is occurring mostly via the following three reactions:

R1: $C_2H_5OH \rightarrow C_2H_4 + H_2O$

R2: $C_2H_5OH \rightarrow CH_2OH + CH_3$

R3: $C_2H_5OH \rightarrow C_2H_5 + OH.$

In Ref. [7], the reaction kinetics of reactions R1-R3 were studied by solving a thermal multichannel master equation [7]. Specific rate coefficients were calculated for reaction R1 from RRKM theory and for reactions R2 and R3 from the Statistical Adiabatic Channel Model.

In the present work, the influence of these results from Ref. [7] on the DLR-RG model was investigated. Adjusting the rate coefficients of the DLR-RG with the results of Kiecherer et al. [7] results in predictions of ethanol species profiles closer to the measured ones, see Figs. 1-2, dashed curve; however, the simulations still underpredict the measured decay and growth rates.
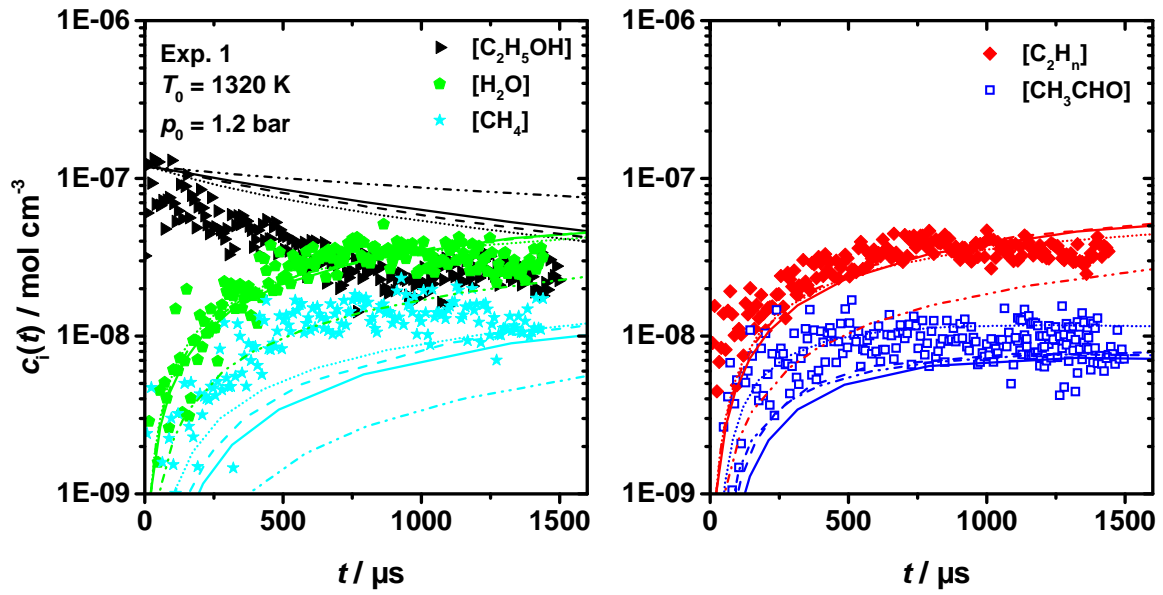
Fig. 1: Comparison between measured (symbols) and predicted (curves) species profiles: Experiment 1 – Tab. 1 [7]. Modeling: present work; solid curves: DLR-RG [5]; dashed: DLR-RG-modified; dotted curves: Marinov [10]; dashed-dotted-dotted curves: Ranzi *et al*. [11].
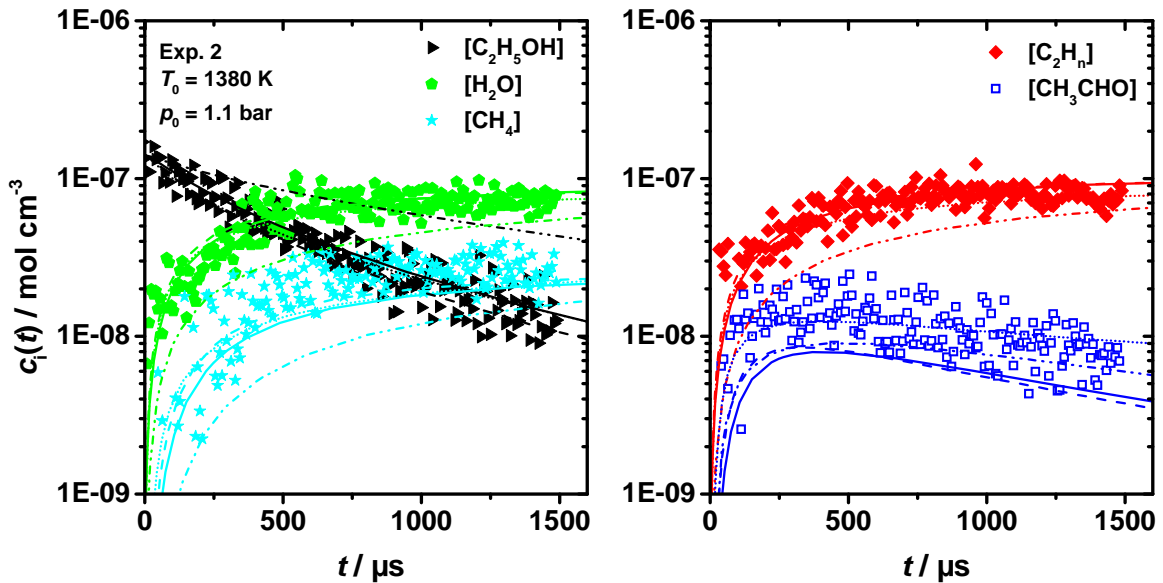

Fig. 2: Comparison between measured (symbols) and predicted (curves) species profiles: Experiment 2 – Tab. 1 [7]. Modelling: present work; solid curves: DLR-RG [5]; dashed: DLR-RG-modified; dotted curves: Marinov [10]; dashed-dotted-dotted curves: Ranzi *et al*. [11].

Experiments performed at elevated pressure

In general, the results obtained at higher pressures are in line with the ones obtained at ambient pressures discussed earlier. As an example, the comparison between calculated and experimentally determined species profiles are shown in Fig. 3, at elevated pressure of 3.6 bar and at T = 1400 K.

Figure 3 illustrates that the predictive capabilities of the model by Ranzi *et al*. seem to improve at higher pressures, compared to the results at ambient pressure.

Reaction flux and sensitivity analysis

Reaction flux and sensitivity analysis were performed to get more insight into the combustion of ethanol, in particular concerning the differences between the DLR-RG model and the model given by Ranzi *et al*., respectively (Figs. 4-5).

The results for the reactant ethanol are depicted in Fig. 4, at T = 1380 K and p = 1.1 bar, for Exp. 2 (Tab. 1). From Fig. 4, as expected, the major destruction channels of C_2H_5OH are (R1 –R3), with (R1) leading to

ethylene and water predicted by both mechanisms as the most important one: The DLR-RG mechanism predicts that 47% of C_2H_5OH has decayed to C_2H_4 (R1) compared to about 38% predicted in the Ranzi mechanism. In addition to these three reactions, less important channels of ethanol decomposition form CH_3CHOH and C_2H_4OH.

Though both mechanisms follow similar pathways, a minor difference is seen with respect to the C_2H_5O radicals included: two isomers are present in the DLR-RG model, i.e. CH_2CH_2OH and C_2H_5O; in the model given by Ranzi *et al.*, these two isomers are lumped as one species, C_2H_4OH. The CH_3CHOH decomposes completely to CH_3CHO.

Also, a small difference exists in the consumption channel of acetaldehyde between the two mechanisms considered. In the Ranzi mechanism, about 75% of acetaldehyde converts to form CH_3CO, whereas in the DLR-RG model, an additional channel forming two isomers CH_2CHO and $H_2(COC.)H$ is included.

Further C_2-consumption pathways are well known and are predicted similarly by both mechanisms with small differences.

A sensitivity analysis was performed for the same experimental conditions, with results shown in Fig. 5, for ethanol (left) and acetaldehyde (right).

Concerning ethanol, both models agree with respect to the type of sensitive reactions and to the sign of their sensitivity coefficients; the relative sensitivities, however, are different. In both mechanisms, the three most important reactions are ethanol decomposition reactions. The Ranzi model predicts a higher sensitivity with respect to the ethanol decay as well as to the H-abstraction reactions. In addition, ethanol concentration is much more sensitive with respect to

acetaldehyde reactions and to methyl radical reactions as well, most probably because of the decomposition of acetaldehyde leading to methyl and HCO. This picture might result in a too slow decay of ethanol as predicted by the Ranzi model.

Concerning acetaldehyde, the differences identified earlier with respect to the lumped C_2H_4OH species and the methyl radical reactions are shown to be of high sensitivity.
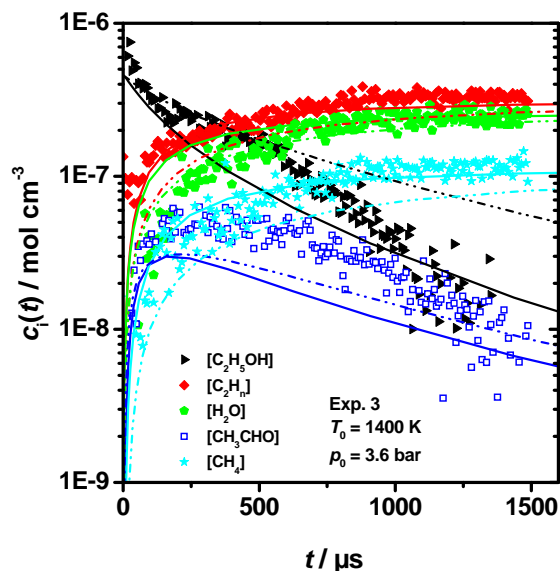

Fig. 3: Comparison between measured (symbols) and predicted (curves) species profiles, Exp. 3 – Tab. 1 [7]. Modelling: present work; solid curves: DLR-RG [5]; dashed-dotted-dotted curves: Ranzi *et al*. [11].
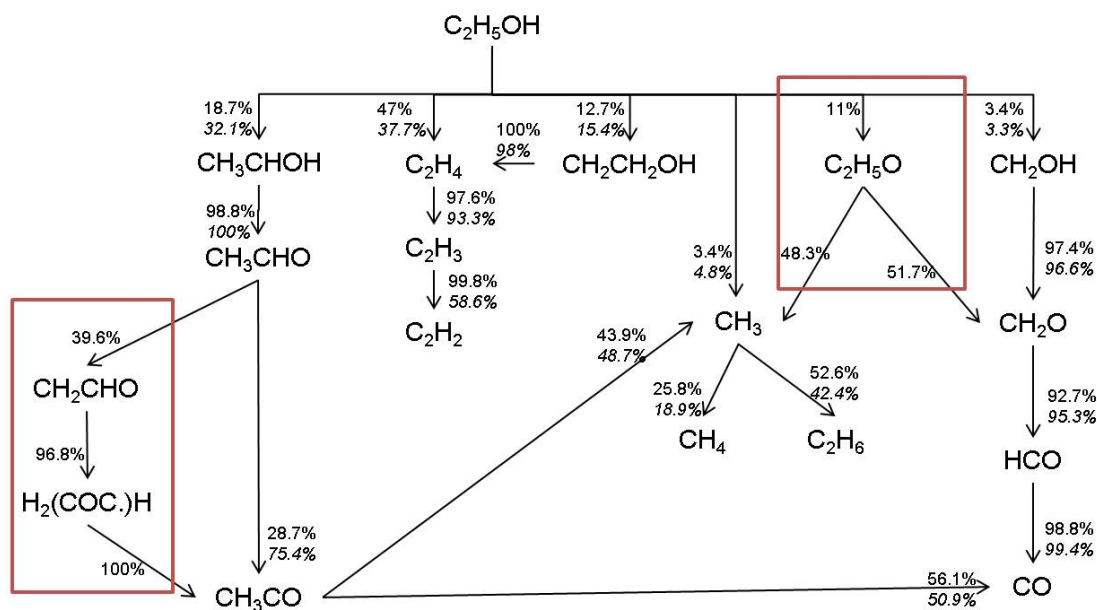

Fig. 4: Ethanol, reaction flux analysis performed at $t = 0.25$ ms for Experiment 2 – Tab. 1 [7]. Two reaction models were used: Plain text: DLR-RG [5]; italics: Ranzi *et al*. [11]. Red highlighted area shows pathways not available in model of Ranzi *et al*. compared to the one of DLR-RG.
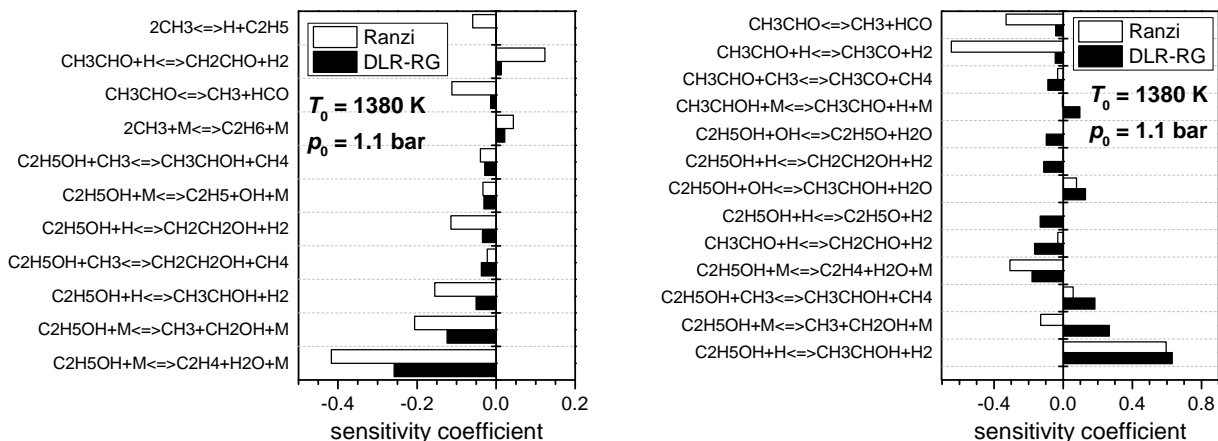
Fig. 5: Ethanol (left) and Acetaldehyde (right): Sensitivity analysis performed at $t = 0.25$ ms for Exp. 2 – Tab. 1 [7]. Calculations with two reaction models: solid bar: DLR-RG [5]; open bar: Ranzi *et al*. [11].

Conclusions

Accurate chemical kinetic models for the design and adaption of combustion applications are needed, to assure clean and reliable energy use of alcohols for electricity and mobility. Being an essential part of those models, understanding ethanol decomposition is of high importance.

Therefore, the performance of a detailed in-house combustion model and two detailed public domain models was studied with respect to five species profiles measured during ethanol decomposition. Experiments were performed in a single pulse shock tube, at temperatures between 1100-1500 K and at pressures of about 1 and 4 bar. Time-of-flight mass spectrometry was used as detection technique.

A good agreement of the species profiles measured was found by the in-house reaction model, with a much better agreement at higher temperatures, for ambient and elevated pressure. Much too slow ethanol decomposition was revealed by the model given by Ranzi *et al.*. This finding might be due to the initial ethanol decomposition pathways and /or due to the acetaldehyde sub model incorporated.

Nevertheless, the results reveal the potential and also the need of optimization of the combustion models of ethanol.

Acknowlegements

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