AUTOIGNITION OF BINARY MIXTURES OF GASOLINE SURROGATES, ETHANOL – ISO-OCTANE BLENDS IN AIR: NUMERICAL AND EXPERIMENTAL STUDY IN A HIGH-PRESSURE SHOCK TUBE

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Abstract. *Ignition delay times were measured in shock-heated gases for a two-component gasoline surrogate comprised of ethanol and iso-octane at a composition of 25% / 75% by liquid volume, with calculated RON/MON numbers of 109/101. The experiments were carried out in stoichiometric mixtures in synthetic air (oxygen 21% - nitrogen 79%) behind reflected shock waves in a high-pressure shock tube. The temperature ranged between 750 – 1200 K, at a pressure of 30 bar. Ignition delay time was determined from CH* chemiluminescence at 431.5 nm measured at a side-wall location. An activation temperature of ~13,272 K was found for the experimental conditions of the shock tube experiments. A detailed chemical kinetics model is proposed for ternary mixtures of gasoline surrogates involving ethanol and primary reference fuels. The kinetics model was obtained by blending the available detailed kinetics models. The qualitative behavior of the ethanol-isooctane mixture investigated in this work was well predicted as well as the behavior of other ignition delay time measurements for pure fuels available in the literature.*

Keywords*: Gasoline surrogates, autoignition, shock tube, detailed kinetics model, ethanol.*

1. INTRODUCTION

Presently, the combustion of practical fuels can only be investigated by experimental approaches. However, the scientific community is moving towards more in-depth numerical approaches as computational resources, numerical methods and chemical knowledge increases. As mentioned by Westbrook et al. (2005), computer modeling has grown rapidly to play a major role in virtually every field of science and engineering. Today it is common to find numerical models attempting to represent combustion process of single hydrocarbon fuels, and depending on the desired quality or target of the results, using either global or detailed kinetics mechanisms. In this direction, many researchers have devoted considerable time studding and proposing global and detailed kinetics models. For example, Griffiths (1995) and Simmie (2003) present reviews for oxidation of pure hydrocarbons.

The number of chemical species that can be present in a real gasoline can be, however, at the order of hundreds, involving saturated and unsaturated hydrocarbons including alkanes, cycloalkanes, alkenes, cycloalkenes, aromatic, ethers and esters, components whose identity and amounts are often unknown (Metcalfe et al. (2007)). The modeling for even a pure component requires reasonable computational resources. The well-known kinetics model for pure iso-octane oxidation of Curran et al (2002) is composed by 857 chemical species allowing 3606 elementary reactions. To think about a detailed kinetics model for a practical fuel involving hundreds of chemical species demands a dramatically increase in the number of elementary reactions, making the problem intractable with current computational capabilities.

Being mindful of the dimension of the problem the scientific community uses a host of methods to have a reliable approach of the problem. One of these is the modeling the combustion of surrogate mixtures.

A surrogate fuel consists of a small number of components that can be used to represent the practical fuel and still predict characteristics of the real fuel. These desirable characteristics may include ignition behavior, burning velocity, viscosity, vaporization, and emission such as carbon monoxide, hydrocarbons, soot and nitrogen oxides (Metcalfe et al. (2007)). The development and modeling of fuel chemistry of gasoline surrogates started with Curran et al. (1998) and Curran et al. (2002). They reported detailed chemical kinetics models of n-heptane and iso-octane covering the parameters used to qualified fuel ignition the Research Octane Number (RON) and the Motor Octane Number (MON). The RON and MON scales are both based on Primary Reference Fuels (PRF); n-heptane (RON = MON = 0) and iso-

octane (RON = MON = 100). Here, the use of surrogate fuels is an approach to make the development of chemical kinetics mechanisms for practical fuels tractable. These kinetics models have been compared to, ignition delay time measurements and other quantities.

Several experimental results of ignition delay time in shock tube have been reported involving PRFs and ethanol. Davidson et al. (2002) reported shock-tube measurements of iso-octane/O_2 mixtures in a temperature range of 1177 to 2009 K, a pressure range of 1.18 to 8.17 bar and equivalence ratios form 0.25 to 2. Hydroxyl radical concentration time histories were reported. Gauthier et al. (2004) reported ignition delay times for n-heptane/air at pressures between 15 – 60 bar, temperatures of 800 – 1350 K and stoichiometric mixture composition. Natarajan and Bhaskaran (1981) reported ignition delay time measurements in a shock tube of mixtures of ethanol/O_2, for pressures of 1.0 and 2.0 bar at higher temperatures of 1300 – 1700 K and equivalence ratios of 0.5, 1.0 and 2.0. Dunphy and Simmie (1991) reported ignition delay times of ethanol/O_2 mixtures at high temperatures (1080 – 1660 K), pressures between 1.8 – 4.6 bar and equivalence ratios between 0.25 – 2.0. Cancino et al. (2009) reports measurements of ignition delay times measured in a high-pressure shock tube for a temperature range of 690 – 1200 K at pressures of 10, 30 and 50 bar for stoichiometric composition of ethanol/air mixtures. More information about experimental results involving ethanol in different experimental results can be found in Cancino et al. (2008).

Concerning numerical studies of binary gasoline surrogate mixtures involving PRFs, Curran et al. (1998) proposed the first detailed kinetics model for n-heptane and iso-octane blends at elevated pressures. This kinetics model was validated against experimental results in a high-pressure flow reactor using both the pure components and their mixtures in a temperature range of 550 – 850 K and at pressures of 12.5 bar. The Curran et al. (1998) PRF model was validated against measured ignition delay times in shock tubes over the temperature range of 690 – 1220 K and at pressure of 40 bar, Good agreement was observed between experimental and simulation results for both pure PRF and their mixtures. Concerning ethanol oxidation, Marinov (1999) proposed the often cited detailed kinetics model for high-temperature ethanol oxidation validated against experimental results of ignition delay time in shock tube from Dunphy and Simmie (1991) and Dunphy et al. (1991) for temperatures between 1300 – 1700 K, a pressure range of 1 – 3.4 bar and equivalence ratios between 0.5 – 2.0. Afterwards, Cancino et al. (2009) upgraded Marinov's ethanol kinetics and proposed a detailed kinetics model for ethanol oxidation in air, at pressures of 10, 30 and 50 bar, and intermediate temperatures of 690 – 1200 K in stoichiometric mixtures.

In this work we propose a detailed kinetics model for ternary mixtures of gasoline surrogates involving PRFs and ethanol. Simultaneously, we report experimental data of ignition delay time of the binary mixture ethanol/iso-octane (25%/75% by volume) at pressure of 30 bar and temperatures between 800 – 1217 K for stoichiometric composition. Figure 1 shows the molecular structure of the three fuels ethanol, iso-octane and n-heptane molecules considered in the detailed kinetics model proposed here.

Ethanol   2,2,4-trimethyl-pentane   n-heptane
                        (iso-octane)
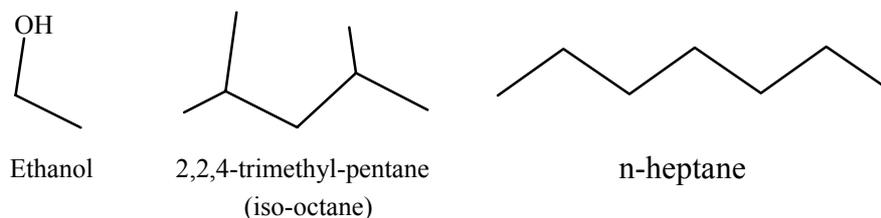
Figure 1. Molecular structure of fuels considered in this work

The proposed gasoline surrogate model is composed by ethanol (oxygenate hydrocarbon), iso-octane (saturated iso-paraffin), n-heptane (saturated n-paraffin).

2. EXPERIMENTS

The experiments were carried out in the high-pressure shock tube at the University of Duisburg-Essen, Germany. This facility, depicted in Figure 2, has an internal diameter of 90 mm, divided by an aluminum diaphragm into a driver section of 6.1 m and a driven section of 6.4 m in length. The driven section is pumped down to pressures below 10^{-2} mbar in between the experiments. Gas mixtures were prepared by injecting liquid ethanol - iso-octane (25%/75%) mixture into a stainless-steel mixing vessel and subsequent complete evaporation and mixing. The total amount of fuel mixture and air was controlled manometrically in order to ensure the desired equivalence ratio. The shock speed was measured over two intervals using three piezo-electric pressure gauges.

Pressure data were recorded with a time resolution of 0.1 μs. The temperature and pressure behind the reflected shock wave were computed from the measured incident shock speed and the speed attenuation using a one-dimensional shock-tube model (shock-tube code of the CHEMKIN package Kee et al. (2000)). The estimated uncertainty in reflected shock temperature is less than ±25 K. The experiments were carried out with synthetic air containing 79.5% N_2 and 20.5% O_2. The ignition was observed by measuring pressure profiles with a piezo-electric gauge (PCB HM 112 A03) located 15 mm upstream of the end flange. Also, the CH* emission at 431.5 nm was selected by a narrow band

pass filter (5 nm HWHM) and detected with a photomultiplier. All ignition delay times shown in this work were determined by extrapolating the steepest increase of the CH* chemiluminescence emission signal to its zero level on the time axis as shown in Figure 2.
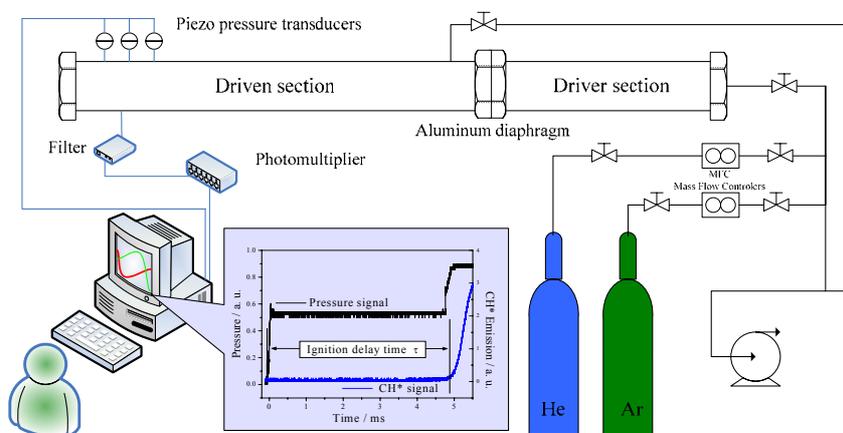
Figure 2. Experimental setup of the high-pressure shock tube facility

The driver gas was mixed in-situ by using two high-pressure mass-flow controllers (Bronkhorst Hi-Tec flow meter F-136AI-FZD-55-V and F-123MI-FZD-55-V). Helium was used as the main component and Argon was added to match the acoustic impedance of the test gas. The required driver gas composition was calculated by a spreadsheet analysis prior to the experiments using equations by Oertel (1966) and Palmer and Knox (1961). Concentrations of 5 to 20% Ar in He were required to generate tailored shock waves.

2.1. Measured ignition delay times

The ignition delay times evaluated from the CH* emission, are listed in Table 1 along with the respective temperatures T and pressures p, for stoichiometric ethanol - iso-octane (25%/75%) / air mixture. At temperatures lower than those shown in Table 1 no ignition was observed within the test time of our experiment (15 ms).

Table 1. Measured ignition delay time in shock tube, stoichiometric ethanol 25% - iso-octane 75% mixtures in air

Φ	T_5 [K]	p_5 [bar]	τ_{ing} [μs]
1.0	1217	30.9	35
1.0	1215	30.8	34
1.0	1169	29.2	58
1.0	1164	30.7	74
1.0	1132	31.9	78
1.0	1059	30.6	404
1.0	1004	30.3	791
1.0	967	31.2	683
1.0	909	30.7	2039
1.0	862	31.1	2097
1.0	809	30.7	N-I

N-I No Ignition

Figure 3 shows the measured ignition delay time for the mixture ethanol / iso-octane (25%/75%) / air mixtures. A regression analysis taking ln(τ) as dependent variable and 1000/T_5 as independent variable was performed obtaining a apparent activation temperature of ~13,273 K
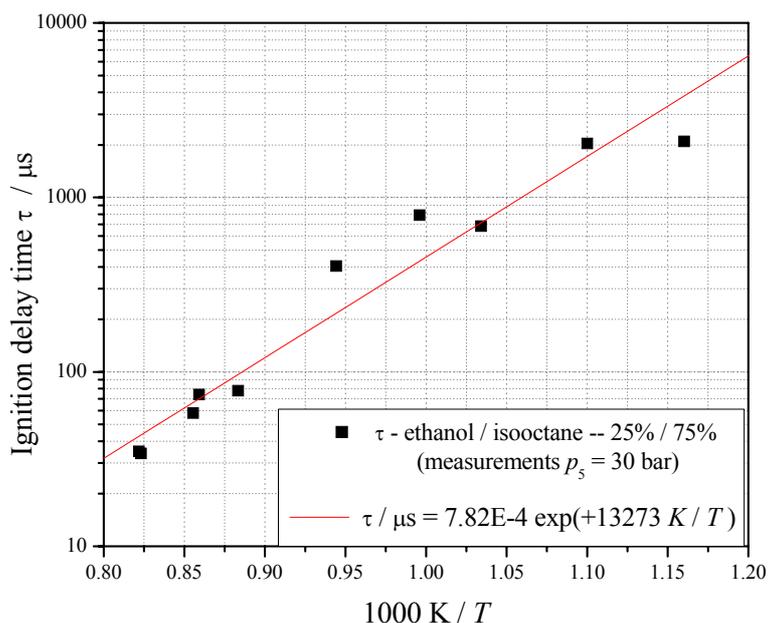
Figure 3. Ignition delay time for mixture ethanol/isooctane (25%/75% by liquid volume) / air.

3. DETAILED KINETICS MODELING

3.1. Blending process

The strategy to tailor the detailed kinetics model requires a sequence of steps that are outlined here:

1. Analyze and potentially adjust the kinetics information of both mechanisms for their use in CHEMKIN.
2. Check the species names in both mechanisms and remove duplicate reactions from the second (minor) mechanism.
3. Add the missing reactions into the main mechanism.
4. Check the thermodynamic data base of the major mechanism and upgrade it with data for the missing species.
5. Test the blended kinetics model with the CHEMKIN interpreter and validate it against measured ignition delay times to make sure that the added reactions for an additional fuel component does not change the behavior of the mechanism in case this component is not present.
6. Optimize the blended kinetics mechanism: Determine the rate-determining route for autoignition via a sensitivity analysis and figure out whether the major reactions have reliable (directly measured) kinetics data.

The blending procedure is time consuming. When two chemical species have the same empirical formula, it is necessary to check their thermodynamic databases by comparing the enthalpy h, heat capacity c_p, and entropy s at several temperatures. If their thermodynamic properties return the same (or similar) values, then both chemical species are identical despite different names or abbreviations used in the original kinetics models. Productivity increases with the use of computational tools. The programs of Rolland and Simmie (2004) were used to compare the kinetics mechanisms and thermodynamic databases.

3.2. Proposed detailed kinetics model for ethanol-PRF blends

A detailed kinetics model for ternary gasoline surrogates involving ethanol, iso-octane and n-heptane is proposed here. The chemical species were selected based on the availability of detailed chemistry in the literature. The starting point was the PRF model of Curran et al. (1998). The chemical kinetics of ethanol oxidation was taken from Cancino et al (2009), which is an upgraded chemistry of ethanol based on Marinov (1999) and Konnov (2000) kinetics mechanisms. Table 2 shows the origin of the sub-mechanisms.

Table 2. Fuels and base mechanisms considered in this work.

	Ethanol and small hydocarbons	n-heptane	iso-octane or 2,2,4-trimethyl-pentane
Chemical formula	C_2H_5OH, $C_1 - C_3$	nC_7H_{16}	iC_8H_{18}
Number of species	136	1034	
Number of elementary reactions	1136	1236	
Validated range	0.9 - 50 bar	40 bar	
	700 - 1200 K	690 - 1220 K	
	$\Phi = 1.0$	$\Phi = 1.0$	
References	Cancino et al. (2009)	Curran et al. (1998)	

4. NUMERICAL SIMULATIONS

The average computational time for each simulation was about ~ 25 minutes, by using a computer Intel Pentium Core Duo Processor, 1.66 GHz with 2.0 GB of RAM. A total of 80 simulations were performed in this work. A FORTRAN source code for the data post-processing of the CHEMKIN output files.

4.1. Results for pure ethanol

Figure 4 shows the numerical predictions of ignition delay time for ethanol-air mixtures at stoichiometric composition, at pressures of 10, 30 and 50 bar for both the Curran PRF model and the proposed detailed kinetics model of this work. These numerical results are compared to experimental conditions from Cancino et al. (2009).
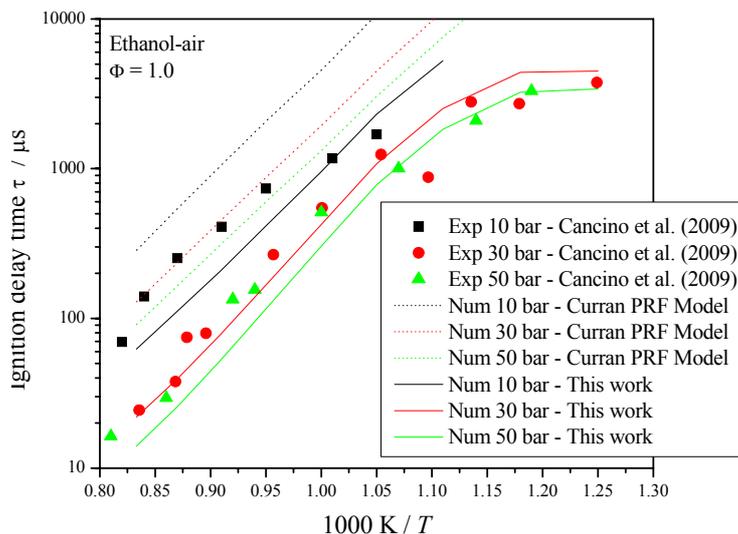
Figure 4. Experimental results from Cancino et al (2009) and numerical predictions of both, the Curran PRF model and of the blended proposed model in this work.

The Curran PRF model was developed specifically for iso-octane and n-heptane fuels and it was expected that the PRF model would fail in the predictions of ignition delay times for ethanol-air mixtures, especially at temperatures below 1000 K. However, the PRF model is sensitive to the pressure dependence of the ignition delay time, as observed in experiments. After adding the ethanol chemistry from recent studies from Cancino et al. (2009) the resulting kinetics model is able to reproduce ignition delay times for ethanol-air mixtures.

4.2. Results for pure iso-octane

Figure 5 shows the numerical predictions of both, the Curran PRF model and the proposed detailed kinetics model for iso-octane / air mixtures at pressures of 16.8 and 49.4 bar, temperatures between 950 – 1200 K and stoichiometric composition. The experimental data was obtained from Davidson et al. (2005).
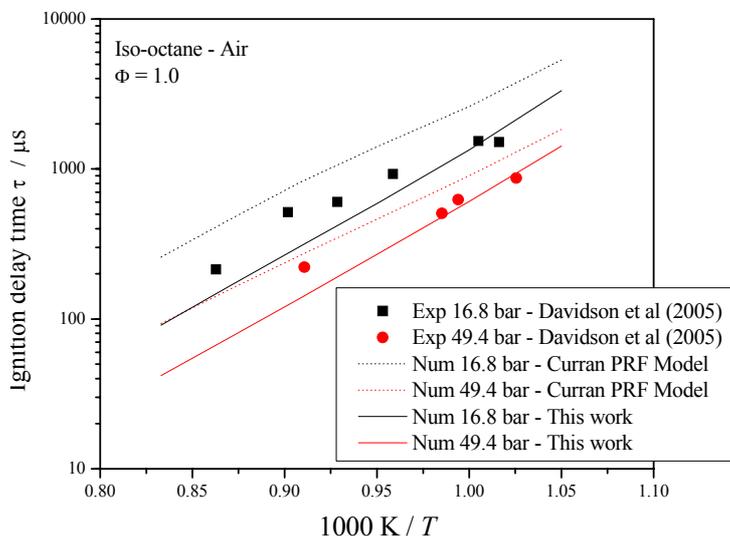
Figure 5. Experimental results from Davidson et al (2005) and numerical predictions of both, the Curran PRF model and of the blended proposed model in this work.

Figure 5 shows that the Curran PRF model overestimates the experimental results, and the discrepancy is more evident at pressures of 16.8 bar. The proposed model slightly underestimates the experimental results at higher temperatures. However, the proposed model captures the general trends of the experiments.

4.3. Results for the gasoline surrogate ethanol / iso-octane (25% / 75%)

Figure 6 shows the numerical and experimental results for the binary mixture investigated in this study.
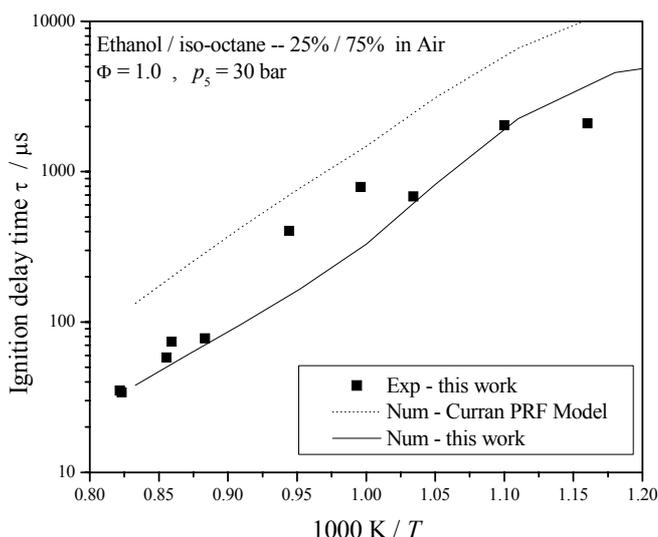
Figure 6. Numerical and experimental results of ignition delay time for ethanol - iso-octane (25%/75%) in air.

The PRF model overestimates the values of ignition delay time in the temperature range of this study. Adding the upgraded ethanol chemistry, the performance of the resulting detailed kinetics model improves. The proposed model underestimates the values of ignition delay time for temperatures about ~1050 K. However, the model captures the general trends of the experiments.

5. CONCLUSIONS

Ignition delay times were measured in a shock tube for a binary mixture comprised of ethanol and iso-octane at a composition of 25% / 75% by liquid volume, with calculated RON/MON numbers of 109/101. The experiments were carried out for stoichiometric mixtures in air behind reflected shock waves in a high-pressure shock tube. Initial reflected shock conditions were varied with the temperature range of 750 – 1200 K at a pressure of 30 bar. An activation temperature obtained by data post-processing of experimental results was found to be ~13,273 K for the investigated conditions at stoichiometric mixture composition. A detailed kinetics model is proposed and validated against our experimental results, and against experimental results of ignition delay times in shock tube for the pure fuels available at literature. The numerical results of ignition delay time of the proposed kinetics model shows good agreement to the experimental data of ethanol and iso-octane available in the literature.

For iso-octane/air mixtures, the Curran PRF model overestimates the experimental results, and the discrepancy is more evident at pressures of 16.8 bar. The proposed model underestimates the experimental results. However, the proposed model captures the general trend of the experiments.

For the binary mixture analyzed in this work, the PRF model overestimates the values of ignition delay time in the temperature range of this study. Adding the upgraded ethanol chemistry, the performance of the resulting detailed kinetics model improves. The proposed model underestimates the values of ignition delay time for temperatures about ~1050 K.

Acknowledgements

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