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C₁-C₄ ALCOHOLS FOR THE TRANSPORTATION INDUSTRY: DETAILED KINETICS MODELS ASSESSMENT IN TERMS OF LAMINAR FLAME SPEED AND IGNITION DELAY TIME

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Abstract. Alcohols are good biofuels and fuel additives due to their reduced ignition propensity, reducing knock propensity in spark ignition (SI) internal combustion engines (ICE). This research gathers published experimental data of C₁ – C₄ primary alcohols to assess published detailed kinetics models in terms of ignition delay time (IDT) and laminar flame speed (LFS). In-house Python routines using Cantera toolkit simulate IDT on a constant volume reactor approach, with conditions ranging 1000/T from 0.6 to 1.2, pressure from 0.9 to 54 bar, equivalence ratio from 0.3 to 2.0, compared to literature experiments of shock tubes and rapid compression machines. The LFS simulations consider laminar flat flames, with and without the Soret and/or radiation effect. Concerning the LFS conditions, the equivalence ratio ranges from 0.7 to 1.5, for atmospheric pressure and 343 K. In terms of IDT, methanol, ethanol and n-propanol showed comparable global apparent activation energies. n-butanol has a lower value probably due to a slight negative temperature coefficient (NTC) for 1000/T > 1.1. Concerning the other exponents on the IDT correlations, pressure has the most consistent one and the anti-knock index has an interesting behavior already pointed out in a previous study. For LFS, there was better agreement with the data for lean and stoichiometric conditions, following a trend already reported in the literature. Yet, only ethanol over-predicts the LFS on the lean side of the plots, while all alcohols over-predict the results on the rich side. Methanol showed velocities higher than the three much similar results for the other alcohols.

Keywords: Detailed Chemical Kinetics, Cantera, Transportation Fuels, Ignition Delay Time, Laminar Flame Speed

1. INTRODUCTION

The transportation industry is currently developing cleaner energy sources, in a myriad of electrification, hybridization, hydrogenation and biofuels. Biofuels have high energy density and lower associated fuelling and distribution infrastructure costs (Vancoillie *et al.*, 2013). In the context of spark ignition (SI) internal combustion engines (ICEs), alcohols from one to four carbons have higher octane ratings than gasoline and can be used as octane boosters or even as neat fuels. Table 1 shows the research octane number (RON), the motor octane number (MON) and the anti-knock index (AKI),

which is the mean between them, for C₁ – C₄ primary alcohols.

Table 1: Octane ratings per fuel

Fuel	MON	RON	AKI	Ref.
Methanol	93	122	107.5	Kubic <i>et al.</i> (2017)
Ethanol	90	109	99.5	Hunwartz (1982)
<i>n</i> -Propanol	89	104	96.5	Ratcliff <i>et al.</i> (2013)
<i>n</i> -Butanol	85	98	91.5	Ratcliff <i>et al.</i> (2013)

The ignition delay time (IDT) is a mean of evaluating the fuels with respect to autoignition and knock propensity. The Arrhenius expression is the simplest mathematical equation used to predict the IDT

$$IDT = A \exp\left(\frac{-E_a}{RT}\right) \quad (1)$$

where A is the pre-exponential factor, E_a the global apparent activation energy, R the universal gas constant and T the temperature. Many published works (Cancino *et al.*, 2011, 2010; Du *et al.*, 2019; Ma *et al.*, 2020; Cooper *et al.*, 2020) reported IDT regressions for neat biofuels or fuel surrogates blended with biofuels, either in the form of Eq. 1 or as the so-called modified Arrhenius expressions, in which dependencies other than temperature are regarded as well (e.g. pressure, species concentration, mixture dilution, stoichiometry, octane rating). Gonini (2022) developed a regression for primary alcohols from one to four carbons considering temperature, pressure, stoichiometry, and anti-knock index. In his literature review, no other correlation regarding all four variables at the same time was found for these fuels. Furthermore, he obtained a correlation by a multivariate and automatized approach, in which multiple linear regressions (MLR) were performed over the database. The database kept changing due to the removal of points that yielded over/undershoots above a certain threshold, thus, the process was done iteratively. The final correlation is described as follows

$$IDT = 10^{0.82 \pm 0.28} \exp\left(\frac{116.7 \pm 0.7}{RT}\right) AKI^{-1.39 \pm 0.14} p^{-0.89 \pm 0.01} \phi^{-0.49 \pm 0.02} \quad (2)$$

where IDT is in μs , temperature (T) is in Kelvin, pressure (p) in bar, anti-knock index (AKI) is adimensional, and stoichiometry (ϕ) is adimensional. Note that the universal gas constant (R) is taken as 8.314×10^{-3} kJ/(mol.K) for this research. This expression is valid for $1000/T$ from 0.6 (1666.66 K) to 1.2 (833.33 K), pressure from 0.9 to 50 bar, equivalence ratio from 0.3 to 2.0, AKI from 91.5 (*n*-butanol) to 107.5 (methanol) and IDT from 21 to 14140 μs . Moreover, it has a high coefficient of determination ($R^2 = 0.991$) with limited over/undershoot (24.4% and -20.0%) and average absolute error (10.5%) between predictions and experiments. Together with these good statistical metrics, the global apparent activation energy showed a plausible value of 116.7 kJ/mol. Nevertheless, the correlation yielded a counter-intuitive negative AKI exponent, meaning that, the higher the AKI , the lower would be the IDT . To broaden the understanding of this counter-intuitive exponent, the laminar flame speed can be an additional variable to study. Therefore, the objective of the present work is to assess published experiments in terms of ignition delay time and the laminar flame speed of primary alcohols from one to four carbons using also published detailed chemical kinetics mechanisms.

2. MATERIALS AND METHODS

2.1 The Cantera suite tools

In this work the Cantera 2.5.1 software was used. Cantera is an open-source suite of tools for problems involving chemical kinetics, thermodynamics, and transport processes (Goodwin *et al.*, 2021). Its functions can automate the chemical kinetics simulation process. Cantera provides types (or classes) of objects representing phases of matter, interfaces between these phases, reaction managers, time-dependent reactor networks, and steady one-dimensional reacting flows. Additional information about Cantera can be found at the Cantera website. In this work, two kinds of simulations of reactive systems were performed: (i) ignition delay time simulation on homogeneous adiabatic constant volume reactor and (ii) laminar free propagating flame speed.

2.2 The numerical and experimental database available in the literature

POLIMI's CRECK Modelling Group developed a detailed kinetics mechanism that was lastly updated by Bagheri *et al.* (2020) (referred as CRECK for simplicity). This mechanism is composed by the following sub-mechanisms and thermodynamic properties, plus several reactions that were updated for the sake of performance improvement: H₂/O₂

and $C_1 - C_2$ (Metcalf *et al.*, 2013); C_3 (Burke *et al.*, 2015); heavier species (Ranzi *et al.*, 2012, 2014); acetaldehyde (Pelucchi *et al.*, 2017); rate rule for H-abstraction reactions (Ranzi *et al.*, 1993); thermochemical properties of hydrogen and syngas cores from Active Thermochemical Tables (ATcT) (Ruscic *et al.*, 2005); and from other important species (Burcat and Ruscic, 2005; Ranzi *et al.*, 2012).

Sarathy *et al.* (2014) followed a manual generation method to develop their mechanism, although it should not be considered new. Essentially, it is an hierarchical assembly of data on reaction mechanisms, rate coefficients, and species thermodynamic and transport properties available in the literature. The sub-mechanisms are: $C_0 - C_2$ hydrocarbon oxidation (AramcoMech 1.3 by Metcalfe *et al.* (2013), which bases its $H_2/CO/O_2$ sub-mechanism on K romn s *et al.* (2013)); C_4 and C_5 alkane and alkene (Healy *et al.*, 2010); methanol (Metcalf *et al.*, 2013); ethanol (Mittal *et al.*, 2014); *n* and *i*-propanol (Johnson *et al.*, 2009), with modifications by Man *et al.* (2014), plus several important low temperature reaction pathways; butanol isomers (Sarathy *et al.*, 2012); *n*-pentanol (Heufer *et al.*, 2012); *i*-pentanol (Sarathy *et al.*, 2013). Table 2 shows the mechanisms in terms of number of elements, species and reactions. Note also that Sarathy *et al.* (2014) has a high-temperature sub-mechanism, described in parenthesis. Since the laminar flame speed data in this study do not lie in this region, only the complete mechanism is considered. For the rest of this work, this mechanism is referred as CCRC (Clean Combustion Research Center, King Abdullah University of Science and Technology - KAUST).

Table 2: Detailed kinetics models used assessing $C_1 - C_4$ alcohols in this work. Numbers within parentheses are relative to the high-temperature sub-mechanism

	CRECK	CCRC
Elements	6	6 (6)
Species	339	687 (354)
Reactions	9781	3674 (2625)
Reference	Bagheri <i>et al.</i> (2020)	Sarathy <i>et al.</i> (2014)

Table 3 shows the papers gathered for the IDT simulations. This database considers low/high pressure shock tubes (LPST, HPST) and rapid compression machines (RCM), but does not consider ignition quality tester (IQT) points, as IQT cannot isolate the kinetics effects from the thermo-fluid-dynamic effects (atomization, vaporization, mixing), masking the contribution of the autoignition stage. The IDT simulations in Cantera use a constant volume perfect stirred reactor (PSR). Also, the IDT criterion is associated with the peak OH mass fraction.

Table 3: Previously published experimental data for ignition delay time of $C_1 - C_4$ alcohols gathered in this research

Fuel	T [K]	p [bar]	ϕ	Device	Ref.
Ethanol	800-1250	20	1	HPST	Nativel <i>et al.</i> (2021)
Ethanol	650-1250	20-40	0.5-2.0	HPST, RCM	Zhang <i>et al.</i> (2018)
Ethanol	944-1589	1.3-53 ¹	0.5-2.0	HPST	Mathieu <i>et al.</i> (2019)
Methanol, ethanol, <i>n</i> -propanol, <i>n</i> -butanol	1070-1760	2-12 ¹	0.5-2.0	HPST	Noorani <i>et al.</i> (2010)
Methanol	940-1540	1-14.9 ¹	0.5-2.0	HPST	Pinz�n <i>et al.</i> (2019)
Ethanol	650-1220	10-50	0.3-1.0	HPST	Cancino <i>et al.</i> (2010)
Methanol	820-1650	2-50 ¹	0.5-2.0	LPST, HPST, RCM	Burke <i>et al.</i> (2016)
<i>n</i> -butanol	800-1600	1-43 ¹	0.5-1.0	LPST, HPST	Stranic <i>et al.</i> (2012)
Ethanol, <i>n</i> -propanol, <i>n</i> -butanol	704-935	10-30	1.0	RCM	Pelucchi <i>et al.</i> (2020)

¹atm

Concerning LFS, Tab. 4 shows the conditions of each experiment. Note that all of them used a twin counterflow configuration. In Cantera, the correspondent function requires mass flux boundary conditions, that are not described in Veloo *et al.* (2010); Veloo and Egolfopoulos (2011), and the authors no longer keep this information (Egolfopoulos, personal communication). Due to the limited dimensions of the domain, with burners of up to 20 mm in diameter and separated by up to 20 mm, it is possible to neglect curvature effects and assume a flat flame. This way, Cantera no longer needs the unavailable mass flux boundary conditions. In addition, Veloo *et al.* (2010) and Veloo and Egolfopoulos (2011) simulated their flames with PREMIX (Kee *et al.*, 1985), as a freely propagating flame. Also, they accounted for thermal radiation of CH_4 , CO , CO_2 , H_2O and the Soret effects in their simulations. Even though they used a mixture-averaged transport formulation, it is only possible to turn radiation and Soret effects in Cantera using a multicomponent formulation. Therefore, to assess the differences between mechanisms and between turning on or off these effects, each experimental point is simulated as a laminar flat flame under the following set-ups: without radiation and Soret effects, with Soret and with both effects, for both mechanisms, all of them following the multicomponent transport formulation.

Table 4: Previously published experimental data for laminar flame speed of C₁ – C₄ alcohols gathered in this research

Fuel	T [K]	p [atm]	ϕ	Device	Ref.
Methanol	343	1	0.7-1.5	Twin counterflow flame	Veloo <i>et al.</i> (2010)
Ethanol	343	1	0.7-1.5	Twin counterflow flame	Veloo <i>et al.</i> (2010)
<i>n</i> -propanol	343	1	0.75-1.5	Twin counterflow flame	Veloo and Egolfopoulos (2011)
<i>n</i> -butanol	343	1	0.7-1.5	Twin counterflow flame	Veloo <i>et al.</i> (2010)

3. RESULTS AND DISCUSSION

The results are divided into IDT and LFS sections for better understanding. Furthermore, to allow a comparison with Gonini (2022) IDT correlations, the correlations are expressed in the following way

$$IDT = 10^a \exp\left(\frac{E_a}{RT}\right) AKI^b p^c \phi^d \quad (3)$$

where 10^a represents the pre-exponential factor A .

3.1 Ignition delay time simulations

The points from Tab. 3 were limited to $1000/T$ from 0.6 to 1.2 (1666.67 K to 833.33 K), the same range used in Gonini (2022). This large range was possible due to the absence of a negative temperature coefficient (NTC) in this region for alcohols. Besides, pressure ranges from 0.9 to 54 bar, equivalence ratio from 0.3 to 2.0, and IDT from 16 to 312100 μ s. This way, there were 833 experimental points following these criteria, shown in Fig. 1.

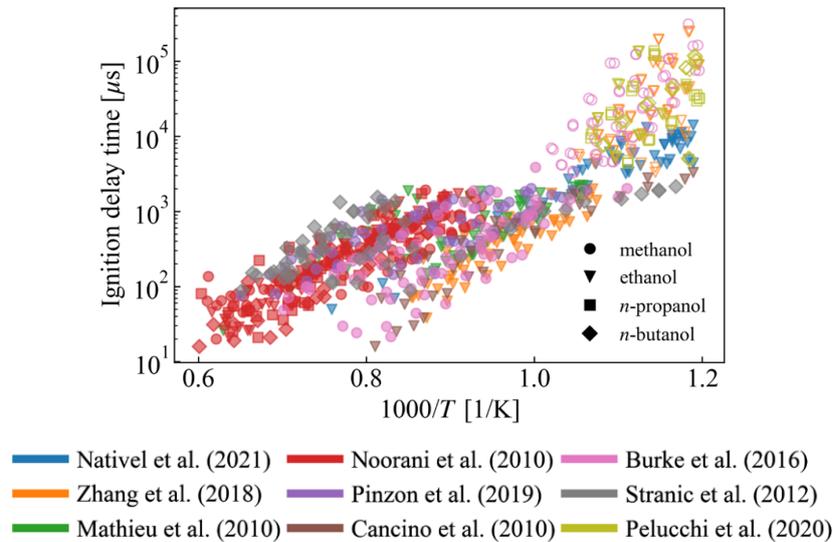


Figure 1: Initial database ignition delay time. Filled markers represent ST data and open markers represent RCM data

3.1.1 Regressions for each fuel treated separately

To avoid overwhelming plots when comparing experiments to Cantera simulations, Fig. 2 shows the IDT per fuel. The best line is displayed for simulations instead of individual points. It is clearer to read but it considers multiple conditions at once. Note that when handling one single fuel, the AKI is always the same and this exponent is zero. Overall, the scattering that occurs in RCM experiments is severely reduced, since the simulations do not account for the extended heat loss, when compared to shock tube experiments. For this reason, the simulations of RCM points mostly underpredict the IDT (although most shock tube points also lie on the underpredicted side). In addition, the absence of heat loss effects seems to reduce the slope of the plots, which represents the global apparent activation energy. Nevertheless, as discussed in Gonini (2022), this visual inspection might be tricky, as the data presents wide ranges concerning four different dependencies (T, p, AKI, ϕ).

For this reason, Tab. 5 shows multiple linear regressions (MLR) for each fuel regarding the four variables. All MLR follow the ordinary least squares (OLS) scheme, referred by Sundberg (1998) as the proper scheme. As previously

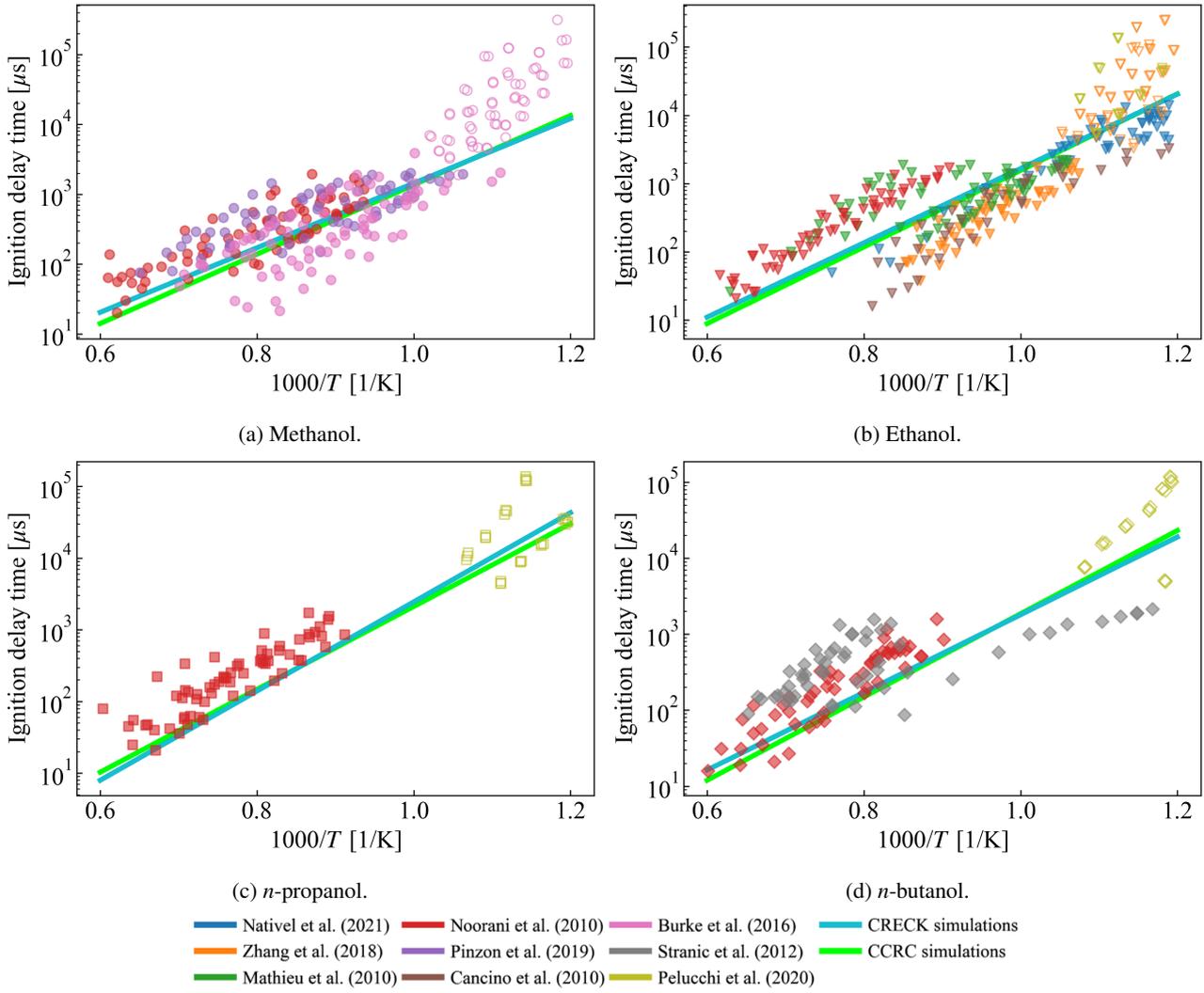


Figure 2: Ignition delay time results comparing Cantera CVR simulations to published experiments. Filled markers represent ST data and open markers represent RCM data.

mentioned, $1000/T$ ranges from 0.6 (1666.66 K) to 1.2 (833.33 K). Concerning pressure, stoichiometry and IDT, the regressions are valid for the following ranges: methanol for $1.0 \leq p \leq 50.0$ bar, $0.5 \leq \phi \leq 2.0$, $20 \leq \text{IDT} \leq 312100$ μs ; ethanol for $1.0 \leq p \leq 54.0$ bar, $0.3 \leq \phi \leq 2.0$, $16 \leq \text{IDT} \leq 249500$ μs ; *n*-propanol for $2.0 \leq p \leq 30.0$ bar, $0.5 \leq \phi \leq 2.0$, $21 \leq \text{IDT} \leq 136400$ μs ; *n*-butanol for $0.9 \leq p \leq 45.7$ bar, $0.5 \leq \phi \leq 2.0$, $16 \leq \text{IDT} \leq 118200$ μs .

Table 5: IDT correlations for each fuel correlation considering T , AKI , p , ϕ

Fuel	Regression	a	E_a	b	c	d	R^2
Methanol	Experiments	-3.04 ± 0.14	142.8 ± 3.6	-	-0.80 ± 0.05	-0.57 ± 0.09	0.876
	CRECK	-3.03 ± 0.02	140.1 ± 0.5	-	-0.94 ± 0.01	-0.52 ± 0.01	0.997
	CCRC	-2.67 ± 0.01	133.8 ± 0.3	-	-0.95 ± 0.01	-0.53 ± 0.01	0.999
Ethanol	Experiments	-2.72 ± 0.12	136.7 ± 2.9	-	-0.99 ± 0.05	-0.62 ± 0.09	0.880
	CRECK	-3.13 ± 0.01	140.9 ± 0.1	-	-0.87 ± 0.01	-0.60 ± 0.01	0.999
	CCRC	-2.91 ± 0.01	136.3 ± 0.3	-	-0.83 ± 0.01	-0.56 ± 0.01	0.999
<i>n</i> -propanol	Experiments	-2.32 ± 0.12	130.2 ± 3.7	-	-0.84 ± 0.10	-0.89 ± 0.18	0.958
	CRECK	-2.84 ± 0.05	136.2 ± 1.4	-	-0.91 ± 0.04	-0.52 ± 0.07	0.994
	CCRC	-3.17 ± 0.04	142.3 ± 1.3	-	-0.83 ± 0.03	-0.42 ± 0.06	0.996
<i>n</i> -butanol	Experiments	-1.68 ± 0.13	112.3 ± 3.5	-	-0.73 ± 0.07	-0.47 ± 0.20	0.901
	CRECK	-2.73 ± 0.05	129.2 ± 1.2	-	-0.78 ± 0.02	-0.28 ± 0.07	0.990
	CCRC	-2.29 ± 0.08	118.4 ± 2.0	-	-0.66 ± 0.04	-0.07 ± 0.11	0.970

Looking at E_a , it is difficult to directly relate a reduced slope with a reduced E_a when regarding multiple independent variables. Noorani *et al.* (2010) regressions based on experiments had the following E_a values for methanol, ethanol, *n*-propanol, and *n*-butanol, respectively: 105.8 ± 2.1 , 134.3 ± 2.9 , 129.3 ± 5.0 , 139.3 ± 5.4 kJ/mol, when converted $R = 1.987 \times 10^{-3}$ kcal/(mol.K), used by the referred author, to $R = 8.314 \times 10^{-3}$ kJ/(mol.K). When based in their simulations, the values change to 126.8 ± 0.4 , 150.2 ± 1.7 , 149.8 ± 1.3 , 160.3 ± 1.7 kJ/mol, respectively. Note that their regressions are dependent upon T , p , ϕ , and D , which is the ratio of argon to oxygen mole fraction. Therefore, while simulations from Noorani *et al.* (2010) always overpredict E_a , CRECK and CCRC yielded much better agreement with this respect. In addition, they reported that methanol had the lowest E_a compared to the other fuels. However, Tab. 5 shows that methanol, ethanol and *n*-propanol have comparable E_a and that *n*-butanol has the lowest one, for both experiments and simulations.

By visual inspection, it seems that for $1000/T > 1.1$ the mechanisms might exhibit a negative temperature coefficient (NTC) for *n*-butanol, which can justify the reduction in E_a . One possible reason is that it is the largest molecule studied in this work. Concerning other works, Ma *et al.* (2020) found 137 kJ/mol for their ethanol experiments and Cancino *et al.* (2010) found 139.3 kJ/mol for ethanol experiments, and 151.6 kJ/mol for their simulations. Therefore, both CRECK and CCRC mechanisms have much better agreement than Cancino *et al.* (2010) simulations, with respect to E_a . At last, the mechanism that is closer agreement in terms of E_a is always closer in terms of the pre-exponential factor (CRECK being better for methanol and *n*-propanol and CCRC for ethanol and *n*-butanol).

Concerning pressure, the mechanisms perform similarly and in good agreement with the experiments. In fact, the pressure exponent is close to the ones from Cancino *et al.* (2010), as they obtained -0.88 and -0.89 for their regressions based on experiments and simulations, respectively. This is expected to happen since IDT mechanisms have some pressure-dependent-Arrhenius reactions with rate constants that exhibit more regular behavior in comparison with temperature-dependent reactions. Other dependencies such as temperature, on the other hand, are more complex, leading to different regions like NTC.

In relation to stoichiometry, the mechanisms reproduce well this dependency for methanol and ethanol. Note that, for *n*-butanol the uncertainty regarding this exponent is larger than its own value for CCRC. The points mostly have ϕ of 0.5, 1.0, 2.0, and sometimes 0.3. These are very few and very different conditions and may lead to some uncertainties. However, it is better to represent ϕ as it is than to scale the data to a common equivalence ratio by a scalar factor (e.g.: ϕ_{old}/ϕ_{new}). In general, the scaling might not be linear between very distant conditions as the kinetics change a lot with ϕ (check LFS results, for instance).

Looking at the metrics, R^2 seems to be low for methanol and ethanol regressions based on experiments, while this is not the case for the other two fuels. This is expected to happen because the first two alcohols have more RCM data, which leads to increased scattering. When compared to regressions based on simulations, R^2 is extremely high, probably because the scattering caused by heat loss is not considered in simulations. Furthermore, the simulations do not account for differences caused by test facilities.

The average absolute error (i.e. relative error to the experiments, without sign), and the over/undershoot might seem alarming; however, a proper IDT study is composed of many points on multiple conditions, and, in the case of the present work, the conditions are very vast and for multiple variables. Furthermore, most studies compare the trends regarding each set of experiments. When analyzing the plots in a more holistic view, the simulations are in good agreement with the experiments.

3.1.2 Regressions for all fuels treated together

To add the AKI exponent to this comparison, it is not simple to gather the four fuels into a single regression. If done in this way, the errors above might be even larger. Therefore, the correlations shown in Tab. 6 are from regressions that underwent the automatized approach developed by Gonini (2022), to drop data that leads to large individual errors to the regression. The first row was already presented by the author. In his previous study, he showed different correlations starting from the same initial database and arriving at the same final database to describe the method. In this work, however, the each correlation has its own final database, since the goal here is to analyze the differences among experiments and mechanisms.

The final databases (Fig. 3) have 275, 209, and 175 points, respectively. The pressure and equivalence ratio exponent are in excellent agreement, as well as the statistical metrics. The mechanisms predicted similar but higher E_a . Nevertheless, this value is close to the ones described in Tab. 5, where each fuel was individually regarded. Finally, the largest difference is with respect to AKI, which presented the counter-intuitive value in Gonini (2022). This time, CRECK yielded a negative but close to zero value and CCRC yielded a positive value. Similarly to ϕ , there are limited AKI bins, which may lead to uncertainties regarding this exponent. In addition, different AKIs mean different fuels and different reaction pathways. Therefore, it is even harder to reduce uncertainties. This study could have considered more fuels but they might not be relevant to the transportation industry. The conclusion is that, even counter-intuitive, this exponent is acceptable as an IDT regression is a simpler representation of detailed mechanisms, for broad conditions regarding multiple fuels.

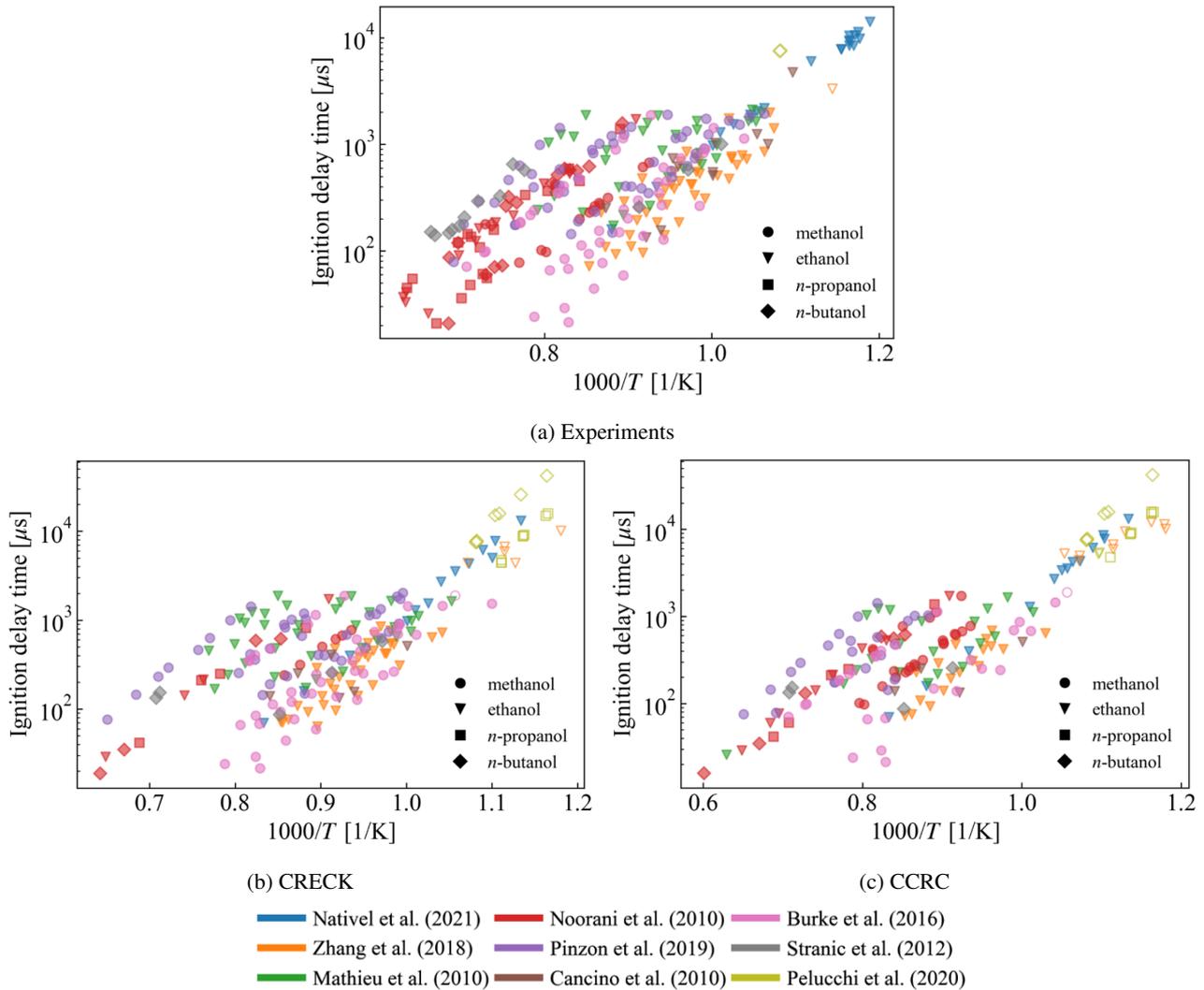


Figure 3: Final database shape after automatized multivariate routine, targeting three different improvements (based on predictions of experiments, and simulations using CRECK and CCRC). Filled markers represent ST data and open markers represent RCM data.

3.2 Laminar flame speed simulations

Figure 4 shows the results for all LFS simulations in comparison with the experiments from Veloo *et al.* (2010) and Veloo and Egolfopoulos (2011). Overall, there is a better agreement with the data for lean and stoichiometric conditions. This trend is similarly reported by Veloo *et al.* (2010), Veloo and Egolfopoulos (2011), Vancoillie *et al.* (2012). Besides, only ethanol over-predicts the LFS on the lean side of the plots, while all alcohols over-predict the results on the rich side.

For all alcohols, the experiments yielded peak LFSs at $\phi = 1.1$. The simulations confirmed this trend except for methanol, which LFS peak occurred at $\phi = 1.2$. This difference was also reported by Veloo *et al.* (2010) when they used the model from Zhao *et al.* (2008). Similarly, Vancoillie *et al.* (2012) reported this event in their simulation at 298 K, using the mechanism proposed by Li *et al.* (2007), following a multicomponent formulation considering only the Soret effect in CHEM1D. Unfortunately, they highlighted that it was not possible to perform the experiment at $\phi = 1.2$.

Methanol showed velocities higher than the three much similar results for the other alcohols, which was also reported by Veloo *et al.* (2010). Concerning the LFS peak magnitude, the experiments show similar peaks LFS magnitudes for ethanol, *n*-propanol and *n*-butanol, 51.0, 51.0, and 50.0 cm/s, respectively, while methanol has a peak LFS of 57.1 cm/s. The simulations ranged from 55.2 to 57.2 cm/s for ethanol, from 50.8 to 52.6 cm/s for *n*-propanol, from 50.4 to 53.3 cm/s for *n*-butanol, and from 57.8 to 62.2 cm/s for methanol. Therefore, the parity among ethanol, *n*-propanol and *n*-butanol was preserved only for the latter two.

Table 7 shows the average absolute error among simulations and experiments. Overall, simulations without both the Soret and radiation effects perform worst. The simulations with Soret are comparable between them but the one with both effects is better in 7 out of 8 times. In addition, CRECK produces always the best results on average, except for *n*-butanol.

Table 6: Summary results for all correlations considering T , AKI , p , ϕ

Regression	a	E_a	b	c	d	R^2	AAE	Oversh.	Undersh.
Experiments	0.82 ± 0.28	116.7 ± 0.7	-1.39 ± 0.14	-0.89 ± 0.01	-0.49 ± 0.02	0.991	10.5%	24.4%	-20.0%
CRECK	-2.90 ± 0.38	139.1 ± 0.8	-0.04 ± 0.18	-0.93 ± 0.01	-0.55 ± 0.02	0.994	10.6%	28.9%	-20.8%
CCRC	-4.40 ± 0.37	140.4 ± 0.8	0.73 ± 0.18	-0.94 ± 0.01	-0.49 ± 0.02	0.995	9.8%	25.1%	-20.5%

Table 7: Average absolute error per simulation [%]. R and S stand for radiation and Soret effect, respectively. + and - stand for turning these effects on or off

Fuel	CRECK			CCRC		
	R-S-	R-S+	R+S+	R-S-	R-S+	R+S+
Methanol	5.9	5.7	5.8	10.6	8.7	8.4
Ethanol	14.3	12.4	12.2	15.4	13.5	13.2
<i>n</i> -propanol	12.2	10.9	10.7	12.8	11.3	11.1
<i>n</i> -butanol	9.9	8.2	8.0	5.4	4.6	4.4

4. CONCLUSION

This work gathered published ignition delay time (IDT) and laminar flame speed (LFS) experiments for C₁-C₄ primary alcohols (i.e., methanol, ethanol, *n*-propanol, and *n*-butanol) and assessed them with also published detailed chemical kinetics mechanisms. The chosen mechanisms, referred as CRECK and CCRC, were developed by Bagheri *et al.* (2020) and Sarathy *et al.* (2014), respectively.

Concerning IDT, the Cantera simulations considered a constant volume perfect stirred reactor. The results were compared in the form of ordinary least squares (OLS) multiple linear regressions (MLR), regarding the influences of temperature, pressure, stoichiometry, and anti-knock index. In general, the IDT correlations based on simulations produced good results when compared to the ones obtained using the experimental database. They reduced the scattering caused by heat loss in rapid compression machines and the test facilities inherent differences and yielded a higher coefficient of determination (R^2). In addition, they were in good agreement concerning the global apparent activation energy (E_a) and pressure. Even for different fuels, the pressure exponent is consistent. This might be due to a more regular behavior of pressure-dependent-Arrhenius reactions and their rate constants in comparison with other factors such as temperature. Regarding the equivalence ratio exponent, it is good but suffers a bit due to the limited number of bins ($\phi = 0.3, 0.5, 1.0, 2.0$), and it is better represented this way than suppressing the exponent and rescaling the data to a common condition.

Comparing the fuels, methanol, ethanol and *n*-propanol had similar E_a , with *n*-butanol below them. In fact, some negative temperature behavior was visually identified for $1000/T > 1.1$ for *n*-butanol and may justify this difference. However, according to Noorani *et al.* (2010) regressions based on experiments and simulations, from C₁ to C₄, E_a was expected to be crescent but this was not verified.

Finally, the counter-intuitive anti-knock index (AKI) exponent reported by Gonini (2022) might be due to a combination of factors. An IDT correlation, regardless of the number of independent variables, is a single mathematical equation and it is simpler than all the information given by a detailed mechanism. It is a very convenient representation but should be considered alongside the ranges of validity of each variable and the types of fuel. Since both mechanisms delivered similar correlations with respect to E_a, p, ϕ and strong statistical metrics, the AKI exponent might be due to the limited number of bins (only four fuels). Since the goal is to include only relevant neat transportation biofuels, an option to further investigate this work is to perform one-dimensional numerical simulations on engine cycles.

In terms of LFS, the simulations considered a laminar flat flame. The results on the lean-to-stoichiometric side were in good agreement with the literature, while on the stoichiometric-to-rich side the simulations over-predicted the results. This is in agreement with Veloo *et al.* (2010), Veloo and Egolfopoulos (2011), Vancoillie *et al.* (2012). It should be noted, however, that for ethanol the results were over-predicted for the whole range of equivalence ratio. Methanol had the highest LFS and the other three remained relatively comparable, in agreement with the literature. In terms of overall performance, CRECK performs better except for *n*-butanol, and simulations without the Soret and the radiation effect performed worse than the others.

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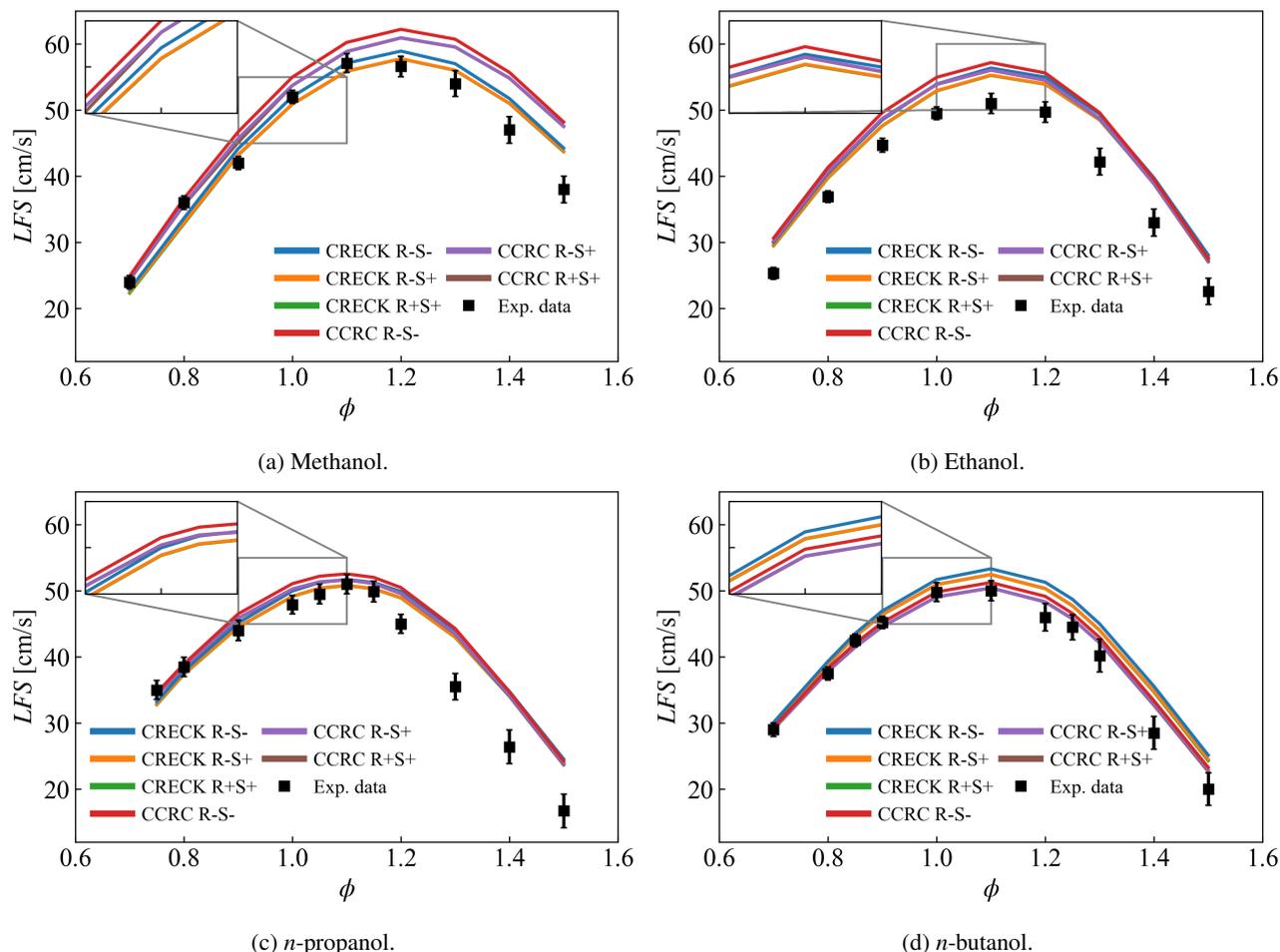


Figure 4: Laminar flame speed results comparing Cantera laminar flat flame simulations to twin counterflow experiments Veloo *et al.* (2010) and Veloo and Egolfopoulos (2011), at 1 atm and 343 K. R and S stand for radiation and Soret effect, respectively. + and - stand for turning these effects on or off.

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