

## ENC-2022-0255

# SURROGATE FUELS FOR BIOFUELS: A LITERATURE REVIEW AND NUMERICAL ASSESSMENT UNDER INTERNAL COMBUSTION ENGINE-LIKE CONDITIONS

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**Abstract.** *It is believed that adding some fuel components to a surrogate model of biofuel can improve the attribution of properties of these chains of components for each major category. In this work, some approaches for non-intuitive analysis of biofuels representation will be reviewed. An extensively literature review on biofuels is presented and discussed in terms of physical-chemical properties including a large database of ignition delay time experimental data. The review involves the detailed kinetics models available in the research community for the surrogates, key details as number of chemical species as well as chemical and physical behavior are pointed out during the analysis, connecting with the fuels applications in internal combustion engines. Details about the kinetics mechanism validation in experimental set-ups, as well as pressure, temperature and stoichiometry parameters were summarized and presented. Numerical simulation using the CANTERA tools kits was then performed in order to assess the numerical behavior of the reviewed kinetics models for ethanol methyl-decanoate, methyl-5-decanoate and methyl-9-decanoate in order to compare against the literature under engine-like conditions in terms of pressure, temperature and stoichiometry. This work comes to aid researchers of combustion for understanding information about biofuels combustion and chemistry kinetics current available. Opening space for new simulation and projects for improving current IC engines technologies for the new fuel possibilities.*

**Keywords:** *Biofuels for the transportation industry, Fuel surrogates, Detailed kinetics models, Cantera, Internal Combustion Engines*

## 1. INTRODUCTION

The need of future societies for continuous mobility necessitates the search for alternatives for fossil energy sources (Kerschgens *et al.*, 2015). The rapid increase of energy demand and consumption as a result of the increase in global population and industrial developments in recent decades has led to the accelerated depletion of non-renewable fossil fuel reserves and related adverse environmental impacts. In particular, the excessive utilization of fossil fuels for energy gen-

eration and transportation applications produces harmful emissions, like carbon dioxide ( $CO_2$ ), nitrogen oxides ( $NO_x$ ), hydrocarbon (HC), and particulate matters (PM), which lead to global warming and are detrimental to the health of human beings (Ran *et al.*, 2022). The fuels of bio-origin can provide a feasible solution to this worldwide petroleum crisis. Gasoline and diesel-driven automobiles are the major sources of greenhouse gases (GHG) emission (Kessel, 2000), (Cao, 2003), (Diniz, 2007). Besides the fact that biofuels are renewable, research has also shown that diesel engines operating with biodiesel produce less CO, unburned hydrocarbons, and particulates (Dooley *et al.*, 2008).

Brazil is a pioneer in the production and use of biofuels, such as ethanol and biodiesel, and this proposal contributes to the goals of mitigating impacts on the environment, including the reduction of the production of greenhouse gases, and the development of a sustainable chain of production and consumption of renewable fuels for transport and stationary power generation. Additionally, Brazil has an extensive infrastructure for the production and distribution of ethanol, which positions it as one of the largest ethanol producers in the world. In the domestic market, the fuel composed of a mixture of ethanol and gasoline is commercially available in a proportion of about 27% ethanol, however, it is used in FLEX engines in different proportions, ranging from 27% ethanol to 100% ethanol. Although the production of engines adapted to run on ethanol has been around for over four decades, basic research into the combustion characteristics of ethanol and ethanol/gasoline blends has not kept pace with the progress of engine control technologies. Thus, much of the development of engines and combustion technologies has been based on empirical procedures, which are limited by cost and development time criteria. For example, the use of ethanol in compression ignition engines (Diesel cycle) has not yet reached the market, as engine development has focused on spark ignition systems for "light" fuels, typical of Otto cycle engines (ethanol and mixtures of ethanol and automotive gasoline). In Brazil, the current diesel is B10, which has 90% of diesel and 10% of biodiesel (ANP, 2021); this fuel has a lower calorific value that is lower compared to pure diesel; this requires changes to engine operating points.

Biodiesel is a renewable fuel source suitable for use within the current transport sector infrastructure, as it shares similar physical properties with conventional crude-oil-derived fossil fuels (Agarwal, 2007). Biodiesel can be blended in any proportion with mineral diesel to create a biodiesel blend or can be used in its pure form. Just like petroleum diesel, biodiesel operates in compression ignition (diesel) engine, and essentially require very little or no engine modifications because biodiesel has properties similar to mineral diesel. It can be stored just like mineral diesel and hence does not require separate infrastructure (Agarwal, 2007). In addition to the combustion quality expressed by the cetane number, many other properties are equally important to demonstrate the suitability of biodiesel as an alternative fuel. Heat of combustion, pour point, viscosity (kinematics), oxidation stability and lubricity are among the most important of these properties (Knothe, 2006).

It is important to underline that the basic constituents of diesel, as well as their composition, are not constant, since several variables such as the place of origin of the source of crude oil, the refining operations, the standards adopted and even the season, and so on, may cause difference in the composition of the fuel, making it difficult to understand the engine's overall emissions mechanism (Qian *et al.*, 2018). Many research reports in literature concern the optimization of surrogate formulations to emulate fossil diesel by using several selected properties including cetane number, density, calorific value, viscosity, distillation curve, boiling point, lower heating value (LHV), etc (Qian *et al.*, 2018), (Poon *et al.*, 2016), (Lahane and Subramanian, 2015). The chemical structure of biodiesel is considerably different in comparison to traditional fuels and therefore there is much need of fundamental studies to generate the basic data with regard to their oxidation mechanism (Shafagh *et al.*, 2011).

What is known as biodiesel is a mixture of alkyl esters produced by a process of transesterification of various plant oils. The biggest reason that vegetable oils and animal fats must be converted to alkyl esters is the kinematic viscosity, which in biodiesel is much closer to that of petroleum diesel. The high viscosity of non-transesterified fatty materials leads to serious operational problems in diesel engines, such as the occurrence of deposits in various parts of the engine (Knothe, 2006). Because the carbon contained in biodiesel has been derived from  $CO_2$  already present in the atmosphere, it can be said to be a carbon-neutral fuel (Dooley *et al.*, 2008). As typical biodiesel components consist of alkyl chains that are 10–20 carbon atoms in length (Graboski and McCormick, 1998), generally in groups of n-paraffin, olefins with smaller amounts of oxygenates and i-paraffins (Ripfel-Nitsche *et al.*, 2007), (Schablitzky *et al.*, 2011). This makes it extremely challenging to compose a chemical model that can incorporate oxidation paths for all the components present (Malik *et al.*, 2013). As so the study is difficult from an experimental point of view and their simulation is currently too complex an undertaking. A common approach used to circumvent this problem is to select a surrogate molecule that represents the chemical properties of the real fuel to be studied (Pitz *et al.*, 2007), (Dooley *et al.*, 2008). Since the mechanism usually have an hierarchical assembly process some of the larger biodiesel molecules are very much the latest frontier from numerical fuel chemical models.

Another form of biofuel is ethanol and others from the alcohol family. There are several reasons to investigate the combustion of ethanol. In summary, there is a need for (i) alternatives to conventional hydrocarbon fuels, especially from renewable sources, (ii) fuels that help to reduce pollutant emissions, and (iii) additives to control engine knock (Cancino *et al.*, 2010). Ethanol is naturally produced by the fermentation of sugars. In Brazil, the addition of ethanol in gasoline has gradually increased over the years, from 10% in the 70's to 27% in 2015 (da Silva Jr *et al.*, 2019).

Table 1: Kinetics databases available in the literature for bio-fuel surrogates

Author	Mechanism	Fuel	Reactions	Chemical species	Experimentally tested in
Davies (2015)	Detailed	ethanol, <i>n</i> -heptane	710	710	Compression Machine
Cancino <i>et al.</i> (2011)	Detailed	Gasoline surrogates: <i>i</i> -octane, <i>n</i> -heptane, toluene, ethanol, <i>di</i> -isobutylene	4959	1126	Shock tube
Cancino <i>et al.</i> (2011)	Detailed	Gasoline surrogates: <i>i</i> -octane, <i>n</i> -heptane, toluene, ethanol	4448	1062	Shock tube
Cancino <i>et al.</i> (2011)	Detailed	Gasoline surrogates: <i>i</i> -octane, <i>n</i> -heptane, toluene, ethanol, <i>di</i> -isobutylene	4959	1126	Shock tube
Cancino <i>et al.</i> (2011)	Detailed	Gasoline surrogates: <i>i</i> -octane, ethanol	4743	1056	Shock tube
Lee <i>et al.</i> (2021)	Detailed	<i>i</i> -hexadecane and <i>n</i> -dodecane			physical proprieties
Szymkowicz and Benajes (2018)	Detailed	<i>n</i> -hexadecane, heptamethylnonane, decahydronaphthalene			physical and chemical proprieties
Sun <i>et al.</i> (2021)	Detailed	<i>n</i> -tetradecane, toluene, methylcyclohexane, and ethanol	386	97	Shock tube
Dagaut and Gail (2007)	Detailed	<i>n</i> -hexadecane, <i>n</i> -propylcyclohexane, <i>n</i> -propylbenzene, and <i>n</i> -decane	2018	262	JSR
Saggese <i>et al.</i> (2013)	Detailed	Methyl-esters, methyl-decanoate, methyl-palmitate, methyl-stearate, methyl-linoleate	21174	582	JSR IDT LFS
Ranzi <i>et al.</i> (2014)	Detailed	Phenol, anisole, guaiacol, catechol, vanillin, acetic acid, butanoic acid, pentanoic acid	17790	492	JSR IDT LFS
Zhang <i>et al.</i> (2018)	Detailed	Ethanol	1004	433	JSR IDT LFS
Pelucchi <i>et al.</i> (2016)	Detailed	Alcohols	9781	339	JSR IDT LFS
Herbinet <i>et al.</i> (2010)	Detailed	Methyl decanoate, methyl-9-decenoate, <i>n</i> -heptane	12070	3299	JSR IDT LFS
Burke <i>et al.</i> (2016)	Detailed	Methanol	1011	173	JSR IDT LFS
Johnson <i>et al.</i> (2009)	Detailed	Propanol	2624	237	IDT
Black <i>et al.</i> (2010)	Detailed	Propanol	1399	234	IDT
Sarathy <i>et al.</i> (2012)	Detailed	Butanol isomers	2346	431	IDT
Johnson <i>et al.</i> (2009)	Detailed	<i>i</i> -propanol	3010	531	IDT
Wu <i>et al.</i> (2021)	Skeletal	Biodiesel	1019	187	IDT
Chang <i>et al.</i> (2015)	Skeletal	Biodiesel	172	60	IDT
Stagni <i>et al.</i> (2016)	Skeletal	Biodiesel	2904	177	IDT

To minimize the time and cost of better understanding the combustion processes in modern state of the art engines fueled with these alternative fuels, the availability of reliable and realistic chemical models is the way forward. Yet such models for alternative fuel combustion are scarce especially in the case of biofuels, and those available are not of practical use in terms of computational time since the fuel is complex and likewise the chemical model (Malik *et al.*, 2013). Modeling of novel fuels specifically can help in providing information that has not yet been experimentally decided.

One such detailed mechanism available is from a research group in the Lawrence Livermore National Laboratory (LLNL) (Sarathy *et al.*, 2011), (Westbrook *et al.*, 2007) consisting of 7200 species and 31400 reactions. This mechanism

has been validated for oxidation of 2-methylalkanes from C7 up to C20, essentially representing the composition of biofuels to large extent (Malik *et al.*, 2013).

The recent report from the Intergovernmental Panel on Climate Change has highlighted the contribution that the transport sector makes to the high levels of CO<sub>2</sub> present in the atmosphere and has recommended the global use of biofuels as a means to curtail CO<sub>2</sub> production (Metz *et al.*, 2001). In May 2002, PROBIODIESEL (Brazilian Biodiesel Technological Development Program) was announced with the aim of establishing a regulatory framework for the national development and production of biodiesel. The program was coordinated by the Secretariat of Technological and Commercial Policies of the Ministry of Science and Technology. In addition to the production of soybean oil methyl ester (EMS), the development of soybean ethyl ester (EES) came to be emphasized, because Brazil traditionally has a large national production of sugarcane bioethanol.

### 1.1 HCCI Engine and Biofuels

An important development in recent years has been toward a type of hybrid engine intended to combine the advantages of SI and diesel engines without the problems of either. The basic concept, the HCCI engine, is a premixed, spatially homogeneous charge that is fuel lean and is ignited by piston compression. Because HCCI combustion is premixed and lean and takes place entirely in the gas phase, it avoids the soot production seen in diesel engines, but it uses a high compression ratio that provides high fuel efficiency (Heywood, 2018). By operating very fuel lean, the product temperatures remain relatively low, so production of the nitrogen oxides that lead to photochemical smog is sharply reduced. In fact, the basic form of HCCI uses fuel/air mixtures that are too fuel-lean to be able to support a flame, but because most of the charge ignites and burns nearly simultaneously, there is no flame propagation and therefore no opportunity for knocking operation to occur in HCCI combustion (Westbrook, 2013). HCCI engines have the attractive feature of being suitable for almost any type of fuel, from diesel fuel to gasoline, and they are capable of burning virtually any biofuel with high efficiency and low NO<sub>x</sub> emissions. An interesting extension of this concept is to use two fuels in the same engine, first injecting a small portion of a fuel that ignites easily (i.e., with high cetane number), such as a diesel fuel, followed by a second injection of another, more difficult to ignite fuel (i.e., high octane number). The earlier injected fuel will already be burning when the second injection occurs, which produces a reliable, quite rapid ignition of the second fuel. Reitz and colleagues (Kokjohn *et al.*, 2011) called this strategy reactivity controlled compression ignition (RCCI), and the second fuel in many of their studies has been natural gas or ethanol. The earlier injected, more ignitable fuel can be conventional diesel or biodiesel fuel. The use of multiple injections and the flexibility provided by adjusting the timing of the injections, combined with operation at high compression ratios, can produce very low emissions and high combustion efficiency. The RCCI engine, with its excellent performance characteristics and unusually broad fuel tolerance, is a concept that is likely to grow steadily in importance in the coming years (Westbrook, 2013). In this light the main properties of this different fuel surrogate models should be better understood to improve the current engine technology.

### 1.2 Review of literature

In table 1 it's summarized surrogates containing biofuel components, listed by its authors and informing about how was experimentally tested, the number of reactions and chemical species as the year published. It's presented a large body of works with the effort to make models for biofuel components from alcohols, gasoline to diesel and biodiesel. Using combustion experiments as the shock tube and rapid compression machine for ignition delay time (IDT), burners and jet stirred reactors (JSR) for laminar flame speed (LFS) and rate of consumption of chemical species and also the usage of physical and chemical properties. These models can predict the behavior of the real fuel mixture in computational reactive fluid dynamics (CRFD) simulations. Biofuel are less chemically complex than fossil fuel as it's chemical process generate components with far fewer different molecules than those present in the fossil fuel. This comes as an advantage in selecting key components for compounding a fuel surrogate. The main components chosen for this work are listed and presented in table 2 with its RON and MON values for the gasoline substitutes and the molecular weight with the mass percentage of oxygen content as well as the lower calorific value. Its noticeable in table 2 looking to the RON and MON values how the quality of the alcohols chains presented is up for usage as anti knock deterrent in a SI engine. The hydroxyl radical attached to the carbon chain has a strong covalent connection, thus increasing the activation energy  $E_a$ , and when broken works as a free radical for the combustion propagation. The RON reaches the highest value as 122 for the methanol the smaller molecule and decreases and varies with the different and larger alcohol configurations. To the point that very large molecules as the *di-n*-butyl and larger are ill suited for spark ignition and work best as biodiesel components. They have a higher calorific energy density and a lower oxygen content. Thus requiring more air into the mixture to ignite and being more fuel efficient during the motor operation. A molecule that combines both a good energy density, having a low heating value of 26.7 MJ/kg (Geng *et al.*, 2010), and good knock index is ethanol an easy to obtain product of natural biomass thus having large spread usage in the transportation industry. This properties of biofuel that are interesting for motor applications will be further investigated showing ignition delay times results.

Table 2: Main properties of biofuel components

Species (Formula)	M.Weight	RON <sup>a</sup>	MON <sup>a</sup>	LHV	Oxygen (wt %)
methanol (C <sub>2</sub> H <sub>5</sub> OH)	32.04	122	93	26.7	0.50
ethanol (C <sub>2</sub> H <sub>5</sub> OH)	46.06	109	90	19.83	0.35
<i>n</i> -butanol (C <sub>4</sub> H <sub>10</sub> O)	74.11	105	90	33.08	0.22
<i>n</i> -propanol (C <sub>3</sub> H <sub>8</sub> O)	74.11	105	90	30.68	0.22
isobutanol (C <sub>4</sub> H <sub>10</sub> O)	74.12	105	90	32.96	0.22
2-butanol (C <sub>5</sub> H <sub>12</sub> O)	74.12	105	93		0.22
<i>t</i> -butanol (C <sub>5</sub> H <sub>12</sub> O)	74.12	107	94		0.22
di- <i>n</i> -butyl (C <sub>8</sub> H <sub>18</sub> O)	130				0.12
methyl-5-decenoate (C <sub>11</sub> H <sub>20</sub> O <sub>2</sub> )	184			34.12*	0.17
methyl-9-decenoate (C <sub>11</sub> H <sub>20</sub> O <sub>2</sub> )	184			34.18*	0.17
methyl-decenoate (C <sub>11</sub> H <sub>22</sub> O <sub>2</sub> )	186			34.00*	0.17

<sup>a</sup>: RON(D357) and MON(D908) data from (Park *et al.*, 2015) \*calculated with CANTERA

## 2. METHODOLOGY FOR NUMERICAL SIMULATION USING CANTERA

Values for IDT in different pressures and stoichiometries were gathered for all components listed in table 2. Having the properties and review of literature in mind Ethanol and three large 11 carbon open molecular chains: methyl-decenoate, methyl-5-decenoate and methyl-9-decenoate were chosen to be studied as potential species to be included in a biofuel surrogate. Methyl decanoate has no double bond whereas most esters in biodiesel fuels are unsaturated species like methyl-5-decenoate and methyl-9-decenoate, having double bonds in different positions. The presence of double bonds has an influence on the formation of unsaturated species, which are known to be precursors of soot (Herbinet *et al.*, 2010). Python scripts native to CANTERA version 2.6 (Goodwin *et al.*, 2018) were adapted for the research purposes of this work. The script one simulates the kinetics behavior of a reactive system assuming constant volume condition. The model for ethanol from the combustion chemistry center from the National University of Ireland Galway with 433 chemical species and 1004 reactions was chosen (Zhang *et al.*, 2018). The model is an updated mechanism for ethanol which includes the latest experimental or theoretical work in the literature. Also the model for a biodiesel surrogate mechanisms from the Lawrence Livermore National Laboratory from University of California (Herbinet *et al.*, 2010) was used. The model was developed using the detailed chemical kinetics mechanisms for *n*-heptane and for the methyl-esters, methyl-decenoate, methyl-5-decenoate and methyl-9-decenoate with 582 species and 12070 reactions. For the engine the Skeletal kinetics mechanism of Chang *et al.* (2015) was chosen due to their reduced complexity but good behavior prediction aiding the velocity of computing the ANSYS-CFX™ simulation. To simulate an engine with the software a zero-dimensional reactor network of ideal gas is set with a movable volume to represent the piston that has its movement governed by an user crank speed equation dependent of the internal pressure and forces resulted. An engine is a very complex application for the Cantera that was idealized for chemical applications by using simplified-idealized reactors geometries. So although the software excels in its chemical calculations, several simplifying assumptions and constraints were put in place to make the engine simulation practical and achievable. Like the fuel, which is injected close to top dead center, already gaseous form with a simple inlet valve friction coefficient. Also the combustion chamber having homogeneous conditions like if were a homogeneous charge compression engine and also having no heat or pressure loss. The simulations were done using the species methyl-decenoate and methyl 5 decenoate as representatives of biodiesel and C<sub>10</sub>H<sub>22</sub> as diesel. The power of the engine and key pollutants were evaluated with the increase of biodiesel in the blend, specially in regards to pollution estimations Cantera simulations should excel at.

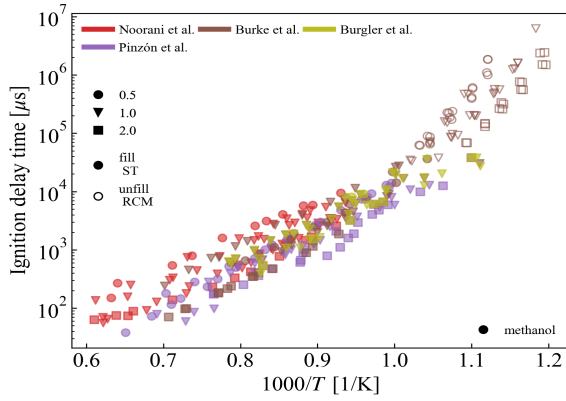


Figure 1: IDT methanol

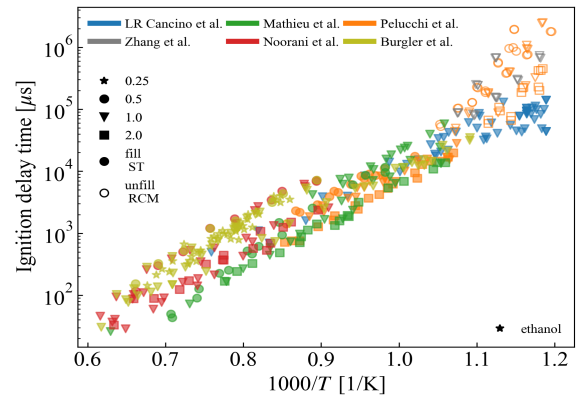


Figure 2: IDT ethanol pressure of 2 bar

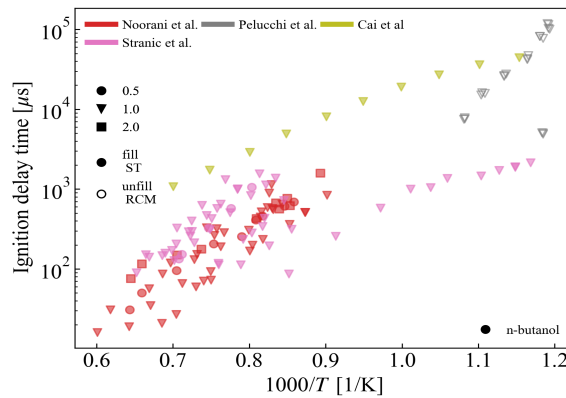


Figure 3: IDT *n*-butanol pressure of 2 bar

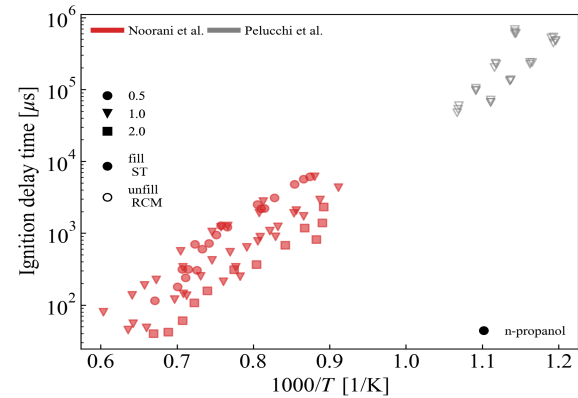


Figure 4: IDT *n*-propanol pressure of 2 bar

### 3. RESULTS AND DISCUSSIONS

The ignition delay time figures were made using experimental results from different authors. For alcohols was found a lot of data in a big range of pressure and temperature so the choice was made to scale all to the common pressure of two bar as means of comparison. We can see the behavior of decrease of IDT for larger alcohol molecules with a decrease of about a order of magnitude for low ethanol temperatures, figure 2, from the methanol figure 1, at same temperatures, and then the same decrease going for *n*-butanol, figure 3, and a further decrease going for *i*-butanol, 2-butanol, *t*-butanol in figures 5, 6 and 7. The last three being very similar molecules and as such showing very similar IDT results. Also all alcohols show a linear relation with temperature and IDT with the exception of low temperatures results done in RCM machines, see figures 1 and 2, since they have more pronounced heat loss effect its know that they don't compare perfectly with ST experiments. Another deviation from the typical linear behavior is in the *n*-butanol figure 3, the graph show first signs of a bent on the low temperature curve, under 1000 K, that indicates the cool flame behavior. It's a well know phenomena that latter causes the NTC in even larger saturated straight carbon chains (Zhang *et al.*, 2016), like the *n*-butanol. It's also noticeable that the *n*-butanol figure 3 has bigger scatter of the data compare to the other alcohols since this work aims to

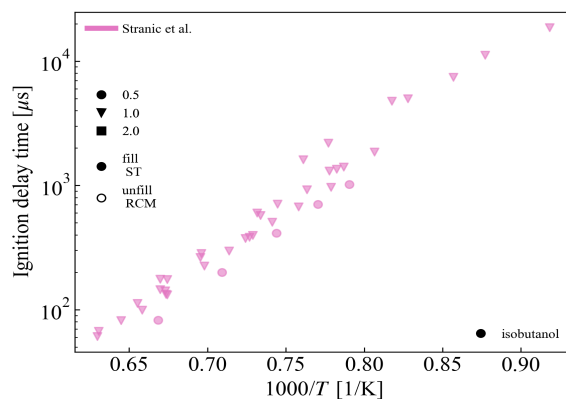


Figure 5: IDT *i*-butanol pressure of 2 bar

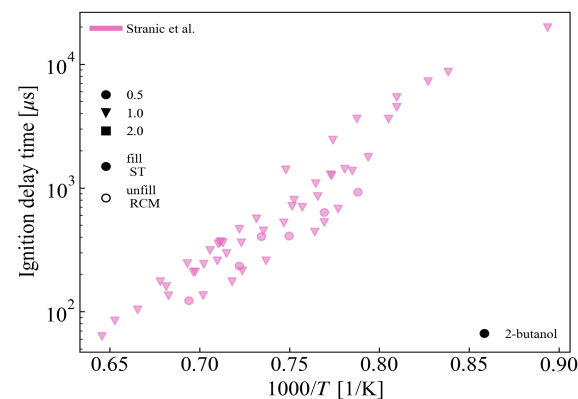


Figure 6: IDT 2-butanol pressure of 2 bar

only compare and evaluate no data from divergent authors was discarded, but is worth noticing it. Finally the behavior of the stoichiometry is shown by the decrease of IDT for higher phi values.

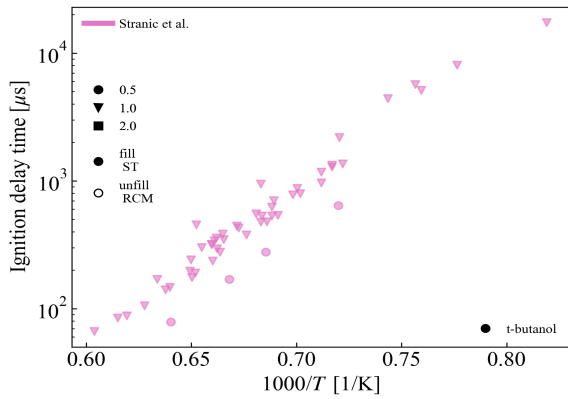


Figure 7: IDT *t*-butanol pressure of 2 bar

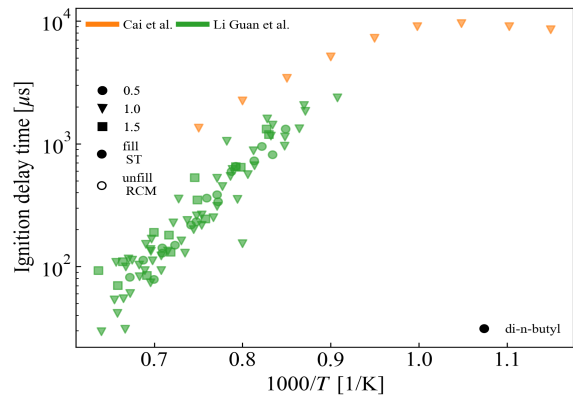


Figure 8: IDT *di*-*n*-butyl pressure of 2 bar

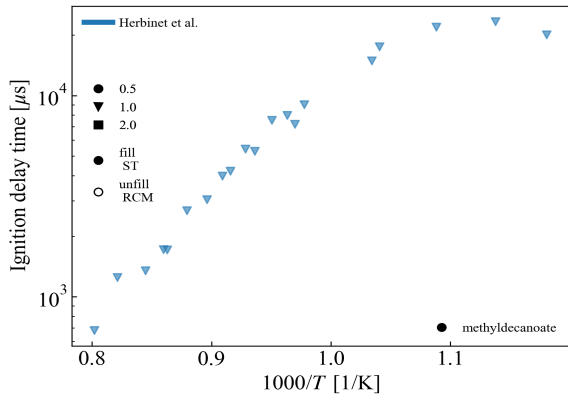


Figure 9: IDT methyldecanoate pressure of 20 bar

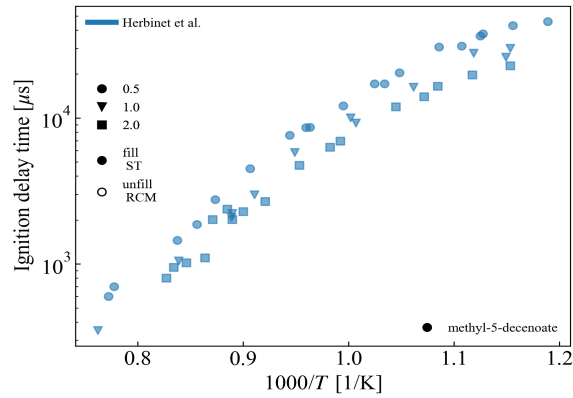


Figure 10: IDT methyl-5-decenoate pressure of 20 bar

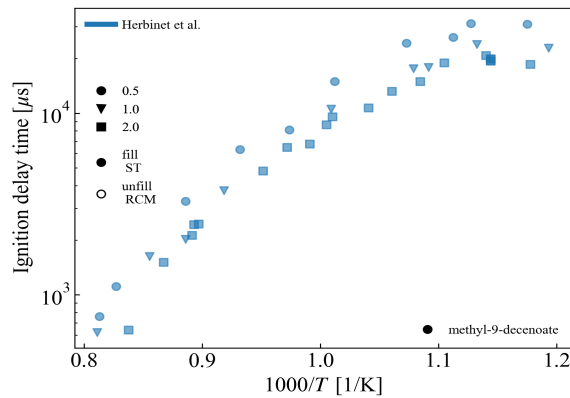


Figure 11: IDT methyl-9-decenoate pressure of 20 bar

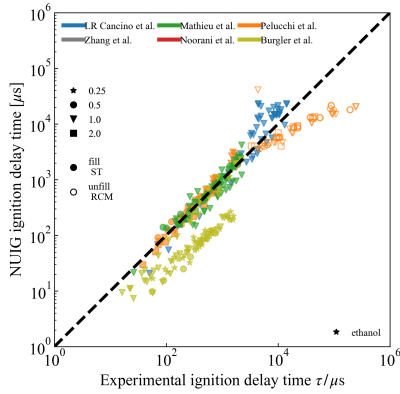


Figure 12: Comparison com values of mechanism of ethanol from NUIG

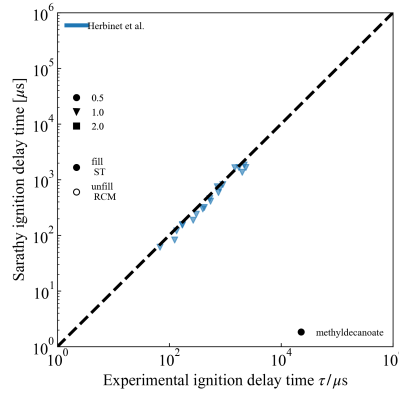


Figure 13: Comparison com values of mechanism of biodiesel from LLNL

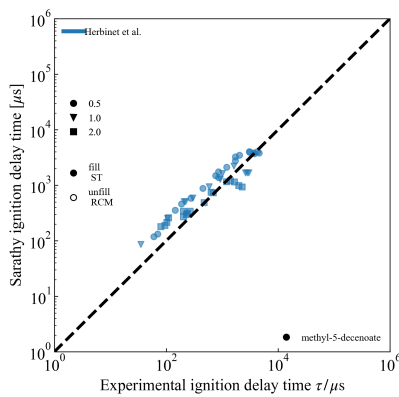


Figure 14: Comparison com values of mechanism of biodiesel from LLNL

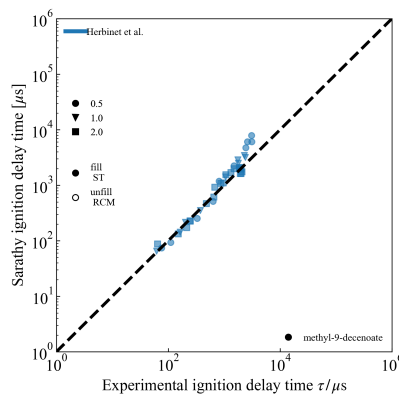


Figure 15: Comparison com values of mechanism of biodiesel from LLNL

It's also worth noticing that there is much more data for smaller molecules and more commonly used and studied biofuels such as ethanol e methanol. The biodiesel graphs were adjusted for a greater pressure of 20 bar since that was better suited for those experimental results, they are studied to work in higher compression rates of diesel cycle. On that note the IDT values are much lower, on figures 8, 9, 10 and 11 with the fuel not resisting very high temperatures like ethanol and methanol can. For the methyldecanoate figure 9 and *di-n*-butyl figure 10 the NTC for lower temperature stands out but even for unsaturated chains like the methyl-5-decenoate figure 10 and methyl-9-decenoate figure 11 this phenomena is visible specially with the contrast of the more linear alcohol graphs. This in line with the literature studied in this work and the applications and proprieties of each fuel. The IDT also lowers with the decreases of the stoichiometry, with the exception of a more scatter pattern in the *di-n*-butyl graph figure 8. Also the unsaturated methyl chains have a small increase in the IDT values.

The numerical results for ethanol figure 12 with the NUIG mechanism was proven very good except for the Burgler results (Bugler *et al.*, 2016) that consistently under predicted the results. Another exception is for low temperatures values, under 920 K, specially for the RCM (Pelucchi *et al.*, 2020) results. Although that is to be expected due to the simulations don't consider heat loss and the low temperature kinetics chemistry being the focus of previous improvements in the mechanism (Zhang *et al.*, 2018). On the other hand the biodiesel mechanism is proven very good for both methyldecanoate figure 12 and methyl-5-decenoate figure 13 with some scatter for methyl-9-decenoate figure 14 but very little. Regarding to the engine simulation in figures 13 and 14 is noticeable how the heat release and expansion power per cylinder decreases with the increase in the biodiesel composition this is to be expected due to the lower calorific value of biodiesel, table 2. Its common practice to offset the decrease in power with a delay in the injection period using biodiesel. This delay is used for attaining the same combustion power output with a fuel that contains slight lower calorific, around 2% lower (Rakshit and Khiraiya, 2017), power than regular diesel. The delay is know in the literature to increase NO<sub>x</sub> pollution (Knothe *et al.*, 2006). This effect associated with biodiesel is related to small differences on the mechanical properties of biodiesel in relation to to conventional diesel like the largest module of comprehensibility and cetane number of biodiesel that together with the injection delay makes the biodiesel reach higher pressures and temperatures in the combustion chamber. Thus this increase in temperature breaks the N<sub>2</sub> bonds activating the NO kinetics. This is already seen in the image 16 even thought we didn't change the injection delay, this would only spark the difference in NO emissions together with the biodiesel difference in proprieties and chemical kinetics.



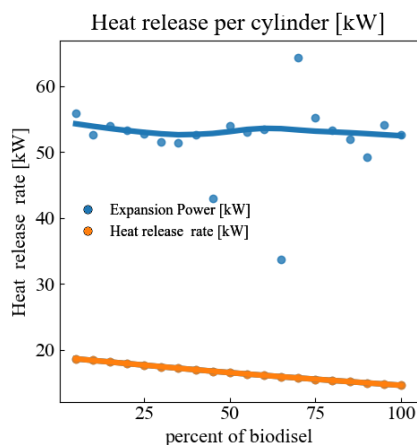


Figure 16: Expansion power and heat release in the cylinder for the different biodiesel and diesel blends

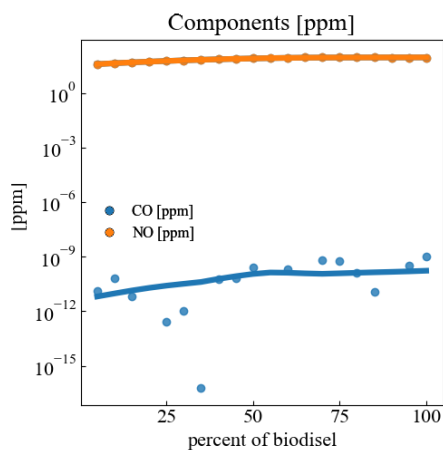


Figure 17: Values of CO and NO in the exhaust of the simulated engine for the different biodiesel and diesel blends

#### 4. CONCLUSION

The present work comes to aid researchers of combustion for searching and understanding information about biofuels combustion and chemistry kinetics current available. Both the mechanism for ethanol from the combustion chemistry center from the National University of Ireland Galway (Zhang *et al.*, 2018) and the model for a biodiesel surrogate mechanisms from the Lawrence Livermore National Laboratory from University of California (Herbinet *et al.*, 2010) was used and evaluated against a large pool of experimental data gather from several different author scaled for a common pressures for enhancing the comparisons. Both mechanism were proven relevant and able to model the IDT behavior of the chemical species chosen. With some under prediction for low ethanol temperatures values, under 920 K, specially for the RCM (Pelucchi *et al.*, 2020) results. Thus it needs to be highlighted that due to the simulations not considering heat loss possibility resulting in errors plus the low temperature kinetic chemistry being the focus of previous improvements in the mechanism (Zhang *et al.*, 2018). On the other hand the biodiesel mechanism is proven very good for both methyldecanoate and methyl-5-decenoate with some scatter for methyl-9-decenoate but very little. As explained in the body of this work this chemical species are important to represent biofuel proprieties in the new fuel surrogates to come. Opening space for new simulation and projects for improving current IC engines technologies for the new fuel possibilities like the homogeneous charge compression ignition (HCCI) engine (Heywood, 2018). In this regard the Cantera simulation done in this work serve as an example on how we can link fuel proprieties, chemical kinetics, combustion science, fluid mechanics to reduce and mitigate fuel pollutants. This tool, as well as improved simulation software, could be further used to make comparisons between different fuel compositions and injection times making easier and faster to test ideas and implement changes. Thus this field of study allows us to come to a step further into adjusting current technology to answer the fossil fuel problematic described in the introduction.

#### 5. ACKNOWLEDGEMENTS

The authors acknowledge the UFSC Joinville IT team (Mr. Kleber Carlos Francisco) for all support given to the LABMCI computer network.

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## 7. RESPONSIBILITY NOTICE

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