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NEGATIVE TEMPERATURE COEFFICIENT - THE INFLUENCE ON FUEL SURROGATE FORMULATION

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Abstract. *Fuels are composed of hundreds of hydrocarbons, making their analysis complex and challenging, computationally or experimentally. An approach employed is the definition of fuels surrogates (mixtures of a reduced number of chemical species), including two or more from each class of hydrocarbons that composes conventional fuels. Normal paraffins produce cold flame/pre-ignition phenomena, characterizing the Negative Temperature Coefficient (NTC) over the pre-auto-ignition period, increasing reactivity, and reducing the ignition period at low temperatures. On the other hand, branched-chain paraffins are more resistant to ignition, which means that reactivity is not affected at low temperatures. In this work, a numerical evaluation was carried out on the influence of normal paraffins in fuel surrogates composition based on the ignition delay times (IDT). Four mixtures were evaluated, involving n-heptane, i-octane, toluene, ethanol, di-iso-butylene, methyl-cyclohexane, and 1-hexane, using a "base surrogate" with 0% vol.% of n-heptane in each and then increasing the percentage by volume on four additional compositions. IDT simulations were performed using in-house PYTHON scripts using the CANTERA toolkit for temperature range from 650 to 1200 K, pressures of 10, 30, and 50 bar at stoichiometry. The simulation results were validated with experimental data available in the literature. The results show that NTC can sometimes be indirectly attenuated by the presence of another class of hydrocarbons (toluene, for example) in the fuel surrogate formulation.*

Keywords: *Negative Temperature Coefficient, Fuel surrogate, Detailed kinetics model, n-paraffins.*

1. INTRODUCTION

With the development of combustion improvement strategies for internal combustion engines and new fuel blends, the need for an in-depth and well-described study of ignition chemistry of fuels is continually increasing. Computational models that include detailed kinetics mechanisms are rapidly progressing to serve as a tool for design and analysis in the field of combustion science and engineering (Cancino *et al.*, 2011). Ignition Delay Time (IDT) dependence can be studied systematically as a function of fuel composition, pressure, temperature, and fuel/air equivalence ratio. On the development and validation of detailed chemical kinetics models for hydrocarbons, many researchers have made extensive use of IDT measurements in shock tubes (ST) and rapid compression machines (RCM), testing, usually, pure

chemical species or mixtures including two or more, all of them called fuel surrogates. High-pressure shock tube (HPST) experiments are extensively used because of the instantaneous heating of the homogeneous air/fuel mixtures, allowing to isolate the effect of chemical kinetics from others (fluid dynamics ones, as an example) (Cancino *et al.*, 2011). Concerning chemical kinetics models, the main difficulty encountered is related to the chemical kinetics behavior of real fuels, such as gasoline. Conventional gasoline has in its composition a combination of several different hydrocarbon classes, the vast majority of which are chemical species from C_4 to C_9 with small percentages of C_{10} and C_{11}. Due to this diverse composition of chemical species, developing a complete chemical kinetics engine simulation using a conventional fuel is a complex problem with current computational capabilities, even using 0D models and then completely intractable by using Computational Reactive Fluid Dynamics (CRFD) (Cancino, 2009). The development of fuel surrogates is a common approach employed to deal with this modeling limitation. Fuel surrogates are compounds made by a mixture of pure chemical components, combining them in percentages that aim to reflect the physical and chemical characteristics of real fuels. Among these pure chemical species, the *n*-heptane and *i*-octane are the reference species for octane rating as well as gasolinesurrogates, being these the Primary Reference Fuels (PRF's).

Several researchers used the research-grade gasoline RD387 for automotive gasoline experiments and numerical studies Abianeh *et al.* (2015) and references therein. RD387 is an $\approx$ 87 anti-knock index (AKI) gasoline (RON = 91, MON = 82.7), without oxygenates, with a H/C ratio of $\approx$ 1.85 blended to represent a customer average regular-grade automotive fuel. In Table 1 can be identified that *n*-alkanes (C_nH_{2n+2}) represent almost 10% of the volumetric composition of RD387 gasoline, being the 4.36% species with seven carbons atoms (*n*-$C_7H_{16} \Rightarrow$ *n*-heptane).

Table 1. Research grade gasoline (RD387) composition - Gas chromatography data from (Piehl *et al.*, 2018).

C#	*n*-alkanes	*i*-alkanes	olefins	naphthenes	aromatics	not clas.	total per C#
C_3	0.112	0.000	0.000	0.000	0.000	0.000	0.112
C_4	2.201	0.306	0.009	0.000	0.000	0.000	2.516
C_5	1.023	4.332	1.527	12.253	0.000	0.000	19.135
C_6	0.697	9.873	2.380	0.830	0.588	0.000	14.368
C_7	4.361	13.183	0.542	1.789	10.489	0.000	30.362
C_8	0.634	11.320	0.270	0.828	7.381	0.000	20.432
C_9	0.248	2.427	0.006	0.224	4.738	0.185	7.826
C_{10}	0.085	0.682	0.000	0.044	2.359	0.230	3.399
C_{11}	0.061	0.092	0.000	0.000	0.773	0.168	1.095
C_{12+}	0.066	0.042	0.000	0.000	0.078	0.569	0.756
Total	9.487	42.257	4.733	15.966	26.405	1.153	100.0

In commercial gasoline *n*-alkanes usually range from *n*-butane to *n*-dodecane. *n*-Alkanes, especially the larger ones, are reactive during low-temperature combustion (Dryer, 2015). Since *n*-alkanes are used to imitate the combustion characteristics of gasoline, it becomes crucial to understand if the surrogate models will accurately model the fuel during low-temperature oxidation, *n*-Alkanes chain length has a tremendous effect on the reactivity due to the cool fame (low-temperature kinetics), and current gasoline surrogate models have poor results when it comes to modeling oxidation behavior in these temperature regions, e.g., (Reuter *et al.*, 2017). One approach to fuel surrogates is to include one or more components from each hydrocarbon class, such as gasoline, a molecular structure where each class can be represented in the surrogate formulation (Metcalfe *et al.*, 2007). *n*-heptane, *i*-octane, toluene, cyclohexane (CHX), and diisobutylene are selected as representatives of n-alkanes, iso-alkanes, aromatics, naphthenes, and olefins to formulate fuel surrogates, according to the chemical composition and carbon range of gasoline (Li *et al.*, 2019). Chemical substances can be found in their pure form or mixtures of species forming blends of two to six compounds in the literature (Cancino *et al.*, 2020). Table 2 shows some of the more common chemical species used as gasoline surrogates by different groups for research purposes.

Numerical simulations are performed using the detailed kinetics mechanisms developed for fuel surrogates, and the validation of these results based on experimental data, performed at several thermodynamic and mixture conditions, temperature (T), pressure (p), and equivalence ratio (ϕ) respectively, usually measured in fundamental combustion test benches: HPST, RCM, jet stirred reactors (JSR), among others. Toluene, *n*-heptane and *i*-octane (and their mixtures) are usually choose as the target chemical species for that validation due to the extensive research performed on them. Table 3 shows some examples of kinetics databases available in the literature.

In this work, a numerical evaluation was carried out on the influence of normal paraffins on the fuel surrogate's formulation based on their IDT. As gasoline surrogates, two mixtures allowing primary reference fuels (PRF's), as well as ethanol, toluene 1-hexene, and methylcyclohexane, were then defined, simulated, and validated by comparison with experimental results available in the literature. The detailed kinetics model chooses for numerical simulations is the reported by Ranzi *et al.* (2012). The influence of the presence of *n*-heptane percentages in the mixtures were analyzed in terms of negative temperature coefficient (NTC). All simulations were performed with in-house scripts developed in PYTHON using the Cantera 2.5.1 toolkit Goodwin *et al.* (2021).

Table 2. Examples of chemical species used to formulate or as fuel surrogates for combustion research

Chemical compound	Other name	Group	Formula	Mol. Weight	RON[a]	MON[a]	Sensitivity
n-Hexane	Hexane	*n*-Paraffin	C_6H_{14}	86.18	24.8	26.0	–1.2
i-Octane	2,2,4-trimethyl-Pentane	*i*-Paraffin	C_8H_{18}	114.23	100.0	100.0	0.0
n-Heptane	Heptane	*n*-Paraffin	C_7H_{16}	100.20	0.0	0.0	0.0
m-Xylene	1,3-dimethyl-Benzene	Aromatic	C_8H_{10}	106.17	117.5	115.0	2.5
Methylcyclohexane	MCH	Naphthene	C_7H_{14}	98.19	74.8	71.1	3.7
Cyclohexane	Hexanaphthene	Naphthene	C_6H_{12}	84.15	83.0	77.2	5.8
Toluene	methyl-Benzene	Aromatic	C_7H_8	92.14	120.1	103.5	16.6
di-iso-Butylene(1)	2,4,4-trimethyl-1-Pentene	Olefin	C_8H_{16}	112.21	106.0	86.5	19.5
di-iso-Butylene(2)	2,4,4-trimethyl-2-Pentene	Olefin	C_8H_{16}	112.21	103.5	86.2	17.3

[a]: values of RON (D357) and MON (D908) from (ASTM Committee D02 - American Petroleum Institute, 1991)

Table 3. Examples of kinetics databases available in the literature for gasoline surrogates

Surrogates	Reactions	Species	Validation	Ref.
n-Heptane *i*-Octane	8157	2115	P, ST FR, JRS	(Westbrook *et al.*, 2009)
Cyclohexane	4269	1081	RCM, JSR	(Silke *et al.*, 2007)
Di-iso-butylene	3783	897	HPST	(Metcalfe *et al.*, 2007)
Low alkylbenzenes	767	150	ST, JSR	(Andrae, 2011)
Toluene	1740	273	LFS, JSR	(Tian *et al.*, 2011)
Ethanol, *n*-Heptane *i*-Octane, 1-Hexene, Toluene Methylcyclohexane	4885	326	HPST	(Cancino *et al.*, 2020)
From C_1 to C_{16}	17847	450	HPST, LFS, JSR	(Ranzi *et al.*, 2012)

P = Pyrolisys, ST = Shock Tube, FR = Flux Reactor, RCM = Rapid Compression Machine
JSR = Jet Stirred Reactor, HPFR = High-Pressure Flow Reactor
HPST = High Pressure Shock Tube, LFS = Laminar Flame Speed

2. THEORETICAL BACKGROUND

2.1 Negative Temperature Coefficient (NTC)

According to (Zhang *et al.*, 2016), the fuel reaction paths are strongly dependent on the fuel structure and significantly affect its reactivity. The reactivity directly impacts the IDT. In addition, the physical conditions to which a mixture is subjected within a reactor, such as pressure and temperature, directly influence the IDT. At low temperatures, the IDT is higher, and as the temperature rises, the IDT presents a tendency to reduce. However, there is a kinetics path for a given class of hydrocarbons which, even with the increase in temperature, the reactivity decreases, which results in the IDT increasing again, presenting an inflection region on the IDT profile as a function of temperature, as the temperature continues to rise this IDT increase reaches a maximum and then decreases again.

For straight-chain hydrocarbons, there is a group of two reactions involving ketones that act differently than expected. For a given temperature range, these reactions cause the increase in temperature to incur a decrease in the reactivity of the mixture. At high temperatures, the most relevant reactions class for the oxidation of *n*-heptane are the unimolecular decomposition of the fuel and fuel-derived radicals, in addition to the abstraction of hydrogen by the set of fuel radicals. On the other hand, at low temperatures, fuel-derived radicals bond with molecular oxygen to form alkyl-peroxyl radicals, with further isomerization, leading to the formation of hydroperoxy-alkyl radicals (Zhang *et al.*, 2016; Curran, 2019a). These hydroperoxy-alkyl radicals contribute significantly to the behavior of the NTC. Due to this additional reaction, the fuel reactivity is reduced. The temperature increase tends to form a more reactive mixture, but in a temperature range, there is an interaction between the molecules, a sequence of reactions that reduces the reactivity, which leads to the increases in the IDT. This behavior is known as NTC (Negative Temperature Coefficient) and is very important for fuel development and formulation. According to (Minetti *et al.*, 1996), *i*-octane and *n*-heptane have a similar self-ignition behavior: a range of NTC associated with a cold flame process and a lower limiting compressed gas temperature, the region in which ignition occurs. However, the authors state that the cold flame region is of greater importance for *n*-heptane than for

i-octane, and the NTC region is extended to higher temperatures in the case of *n*-heptane, amplifying this phenomenon to higher pressures.

The NTC usually occurs at low temperatures (500K < T < 900K), with its identification in HPST and RCM, through the analysis of the pressure or temperature changes that occur before the ignition process. Furthermore, within the simulations, OH concentration peaks before the mixture's auto-ignition show the existence of its partial oxidation, which may be due to the presence of a cool flame or pre-ignition. The time-evolution profile of $OH*$ in HPST experiments can be filtered by chemiluminescence, and then, if observed any change or increase at the beginning of the experiment (before the principal increase), this indicates ignition.

Currently, it is known that the oxidation of *n*-alkanes begin with a unimolecular decomposition, with the formation of small alkyl radicals, or by abstraction of the hydrogen atom (H) during iteration with the O2 molecules. The formation reaction has high activation energy, thus having an important function only at high temperatures, while the latter occurs at both high and low temperatures (Westbrook, 2000; Battin-Leclerc, 2008; Starik *et al.*, 2013; Curran, 2019b). The instability of secondary O_2 addition and subsequent isomerization with the formation of cyclic intermediates, combined with the slow decomposition of H_2O_2 at these temperatures is one of the reasons behind NTC. The occurrence of the NTC is also associated with a change in the $R + O_2 = RO_2$ equilibrium reactions, which favors RO_2 at low temperatures, but changes to favor alkyl R radicals at high temperatures. However, at low temperatures, the oxidation of the hydrocarbons is governed by the initial concentration of fuel, which limits the formation of HO_2, consequently, the addition of the oxygen molecule to the alkyl radicals. At intermediate temperatures, the decomposition of H_2O_2 to $2OH$ is the control rate step, while at the high temperature regime, the $H + O_2 => O + OH$ branching reaction is the dominant reaction. This process described above occurs with linear alkanes due to the absence of steric hindrance to hinder intramolecular isomerization and due to linear paraffin's have more C - H bonds in secondary carbons, a greater proportion of methylene to methyl, than their branched isomers.

2.2 Primary reference fuels: *i*-octane and *n*-heptane

As gasoline is a multicomponent mixture and, with a great diversity of species, the development of substitute mixtures for gasoline with known fuels has great relevance for combustion research. Table 1 shows the percentages of *i*-alkanes and *n*-alkanes in that research-grade gasoline. Therefore, the ignition and burning characteristics studies concerning PRF's are extensive and necessary for better comprehension and characterization of these samples, as well as for the development of new fuels. Simulations with detailed kinetics models show the influence of pressure on the results where, according to the increase in pressure, the ignition occurs faster, which means that the pressure favors the increase in the reactivity of the mixture. This increase in reactivity is due to the increased rate of production of OH radicals from the dissociation of $H_2O_2\ (+M) = OH + OH(+M)$, a pressure-dependent reaction, (Atef *et al.*, 2017).

In these surveys about PRF's, the oxidation of *n*-heptane has been widely studied, and it is representative of a normal alkanes chemical group. It is also a component in the composition of Toluene Reference Fuel - TRF, a representation of a substitute for gasoline in research on combustion processes for internal combustion engines (Zhang *et al.*, 2016). Numerical and experimental investigations on *n*-heptane indicated the oxidation reaction starting close to 560 and 580 K (Ranzi *et al.*, 1995) for pressures above 7 atm, in the low-temperature range. The reduction in reactivity causes the IDT to rise again at low temperatures, in this case, the effect of NTC, which makes sense since it mainly affects straight-chain hydrocarbons. The competition between the reactions of peroxide formation and those that produce less reactive products, such as alkenes or cyclic ethers, is one of the factors responsible for the decrease in alkanes reactivity as the branching level of the molecule increases. The reactivity, in turn, increases as the length of the linear chains increases, in addition, the strong influence of pressure on the IDT is also observed. As observed for *i*-octane, the pressure rise leads to increases in the reactivity of the mixture, however, even with this effect, the NTC effect is observed in the intermediate temperature region, approximately 800 to 950 K.

2.3 Multicomponent Gasoline Surrogate mixtures

Table 4 shows the composition of the mixture of gasoline substitutes to be investigated numerically. In this work, four mixtures involving *i*-octane, methyl-cyclohexane, toluene, ethanol, di-*i*-butylene, *i*-hexane and *n*-heptane were numerically investigated. In each one, the "base mixture" was defined with 0% vol.% of *n*-heptane, and then, four additional compositions for each one were defined increasing the percentage in volume of *n*-heptane according to Table 5.

The six-compound gasoline surrogate GS-BR1 emulates high-performance gasoline. This surrogate has an estimated AKI of 93.8 [RON = 100.6, MON = 87.1] and has been investigated experimentally and numerically in previous work (Cancino *et al.*, 2020). Additionally, the GSBR1 has 27 vol.% ethanol in the composition, modeling a potential Brazilian high-performance gasoline. Table 5 shows the compounds as well as the volumetric percentage on the mixture. Crossing the information of Table 4 and Table 1 it is possible to observe that the surrogate for gasoline GSBR1 allows all the chemical groups present in the research-grade gasoline as well as ethanol.

Table 4. Gasoline surrogate mixtures defined for this work

Primary Reference Fuels *i*-octane and *n*-heptane		**Multicomponent mixtures** ethanol / *n*-heptane / *i*-octane / 1-hexene / MCH** / toluene	
Mixtures	*n*-heptane vol.%	Mixtures	*n*-heptane vol.%
PRF0	100 *	Mixture A	0, 5, 10, 15, 20
PRF60	40 *	Mixture B	0, 5, 10.2, 15, 20
PRF80	20 *	Mixture C	0, 5, 10, 15, 22
PRF90	10 *	Mixture D	0, 5, 11.5, 15, 20
PRF100	0 *		

** MCH: methylcyclohexane

* Experimental data available from literature

Table 5. Multicomponent gasoline surrogate mixtures numerically investigated in this work

Mixture A						**Mixture B**					
Surrogate	Comp. #1 vol.%	Comp. #2 vol.%	Comp. #3 vol.%	Comp. #4 vol.%	Comp. #5 vol.%	Surrogate	Comp. #1 vol.%	Comp. #2 vol.%	Comp. #3 vol.%	Comp. #4 vol.%	Comp. #5 vol.%
n-heptane	0.00	5.00	10.00	15.00	20.00	*n*-heptane	0.00	5.00	10.20	15.00	20.00
toluene	56.25	53.43	50.62	47.81	45.00	ethanol	44.54	42.32	40.00	37.86	35.63
i-octane	31.25	29.68	28.12	26.56	25.00	*i*-octane	42.09	39.99	37.80	35.78	33.67
DIB	12.50	11.87	11.25	10.62	10.00	toluene	13.36	12.69	12.00	1.36	10.69
Total(%)	100	100	100	100	100	Total(%)	100	100	100	100	100
RON	111.6	107.4	103.2	98.8	94.3	RON	109.0	107.1	104.9	102.6	99.9
MON	100.4	97.0	93.4	89.7	85.9	MON	96.2	96.2	95.8	95.0	93.7

Mixture C						**Mixture D**					
Surrogate	Comp. #1 vol.%	Comp. #2 vol.%	Comp. #3 vol.%	Comp. #4 vol.%	Comp. #5 vol.%	Surrogate	Comp. #1 vol.%	Comp. #2 vol.%	Comp. #3 vol.%	Comp. #4 vol.%	Comp. #5 vol.%
n-heptane	0.00	5.00	10.00	5.00	22.00	*n*-heptane	0.00	5.00	11.50	15.00	20.00
i-octane	38.46	36.54	34.62	32.69	30.00	ethanol	30.51	28.98	27.00	25.93	24.41
toluene	32.05	30.45	28.85	27.24	25.00	*i*-octane	33.90	32.20	30.00	28.81	27.12
DIB	16.67	15.83	15.00	14.17	13.00	1-hexene	5.65	5.37	5.00	4.80	4.52
ethanol	12.82	12.18	11.54	10.90	10.00	MCH	7.91	7.51	7.00	6.72	6.33
						toluene	22.03	20.93	19.50	18.73	17.63
Total(%)	100	100	100	100	100	Total(%)	100	100	100	100	100
RON	109.2	107.4	105.3	102.9	99.0	RON	103.9	102.6	100.6	99.4	97.4
MON	95.2	95.6	95.4	94.7	92.9	MON	86.0	86.6	87.1	87.2	87.0

DIB = di-iso-butylene, MCH = Methyl-cyclo-hexane

3. METHODOLOGY

3.1 Numerical Assessment: An In-House Computational Tool

The simulations were performed with an in-house Python script using the CANTERA toolkit. Cantera is an open-source suite of tools for problems involving chemical kinetics, thermodynamics, and transport processes (Goodwin *et al.*, 2021). It is important to attend to the details on how each experiment determines the IDT, which usually is defined by the time between the arrival of the shock wave in the end-wall (in ST experiments) and the time trigger from the emission signal of a radical high reactive species, usually OH^*. Considering the peak as a mark of the IDT both experimentally and numerically, it is a well-accepted practice.

The Python script native to CANTERA was adapted according to the purposes of this work, simulating the kinetics behavior of a reactive system assuming constant volume condition, adiabatic and homogeneous reactor model, and using a detailed mechanism for the chemical kinetics. Thermal ignition was defined as the time of maximum OH concentration throughout the simulation process. To numerically assess the impact of the negative temperature coefficient, given by the percentage of *n*-heptane, on the gasoline substitute, several gasoline substitute formulations were defined and used for the simulations.

3.2 Chemical Kinetic Mechanism, Numerical Validation and Proposed Simulations

In this work, the detailed chemical kinetics model from Ranzi *et al.* (2012) was used for numerical simulations (presented in Table 3), allowing 17847 elementary reactions among 450 chemical species.

The validation of the numerical simulation was based on the numerical predicted IDT and experimental results from

different studies. The first one, from Fieweger *et al.* (1997), the results of IDT were obtained for a set of fuel/air mixtures with different concentration of *n*-heptane and *i*-octane (presented in Table 4), performed in shock tubes in the condition of p = 40 bar, and ϕ = 1.0 for a temperature range from 750 K to 1200 K. Additional conditions were simulated intended to analyze the behavior of the mixtures at different pressures, using 20, 10, and 5 bar. Another comparison for the validation was based on the numerical prediction of IDT with experimental results from the Zhang *et al.* (2016) study, with experiments performed for *n*-heptane/air mixtures, with a fixed pressure varying the equivalence ratio, with ϕ = 0.5, ϕ = 1.0, and ϕ = 2.0, and other condition at stoichiometry and pressure of 6.5 atm and 42 atm for different temperature condition, varying from 650 K to 1200 K.

The proposed simulations for the target surrogates were carried out in the following conditions, temperature range from T = 650 K to 1200 K, pressures of p = 10 bar, 30 bar, and 50 bar, at stoichiometry. This set of conditions results in 68 simulations for each mixture.

4. RESULTS AND DISCUSSIONS

4.1 PRF mixtures

Figure 1 shows the numerical response of the detailed kinetics model from Ranzi *et al.* (2012). The data at 40 bar (Figure 1(a)), at stoichiometry condition was compared to experimental data available in the literature (Fieweger *et al.*, 1997). The model shows a good agreement compared with the experimental results, with a good prediction of the IDT results, representing well the experimental trends. Simulations using different pressure conditions were performed with the interest to observe if the NTC persists at lower pressures, in addition, better understand its behavior. Pressures of 5, 10, and 20 bar were used. It is possible to observe in the results that the NTC manifests itself even at the lowest pressure, 5 bar (Figure 1(d)), and it stands out in the simulations of mixtures with higher concentrations of *n*-heptane. For all pressures evaluated, according to the concentration of *n*-heptane decrease, in direction to the mixture with just *i*-octane, the IDT profile tends to attenuate, reducing the NTC projection. At the pressures of 20 bar and 10 bar (Figure 1(b) and (c)), for the PRF0 the NTC is not observed.

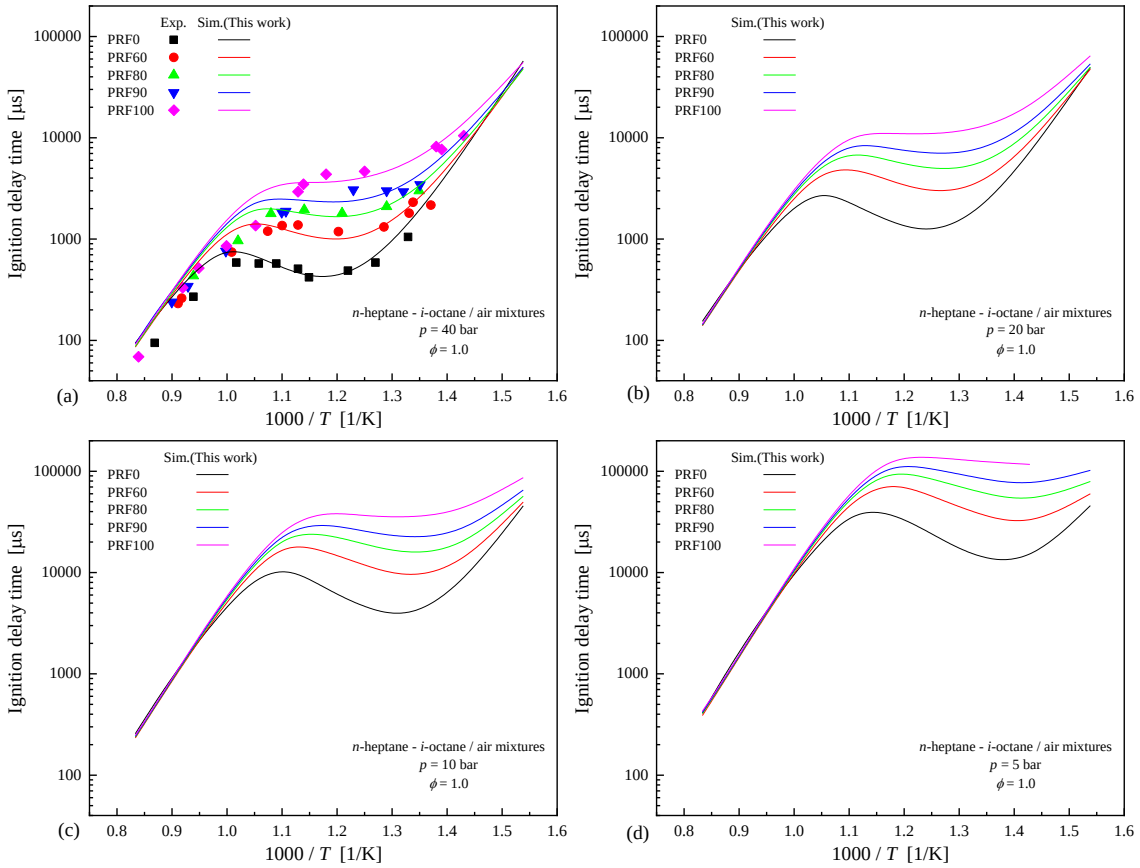

Figure 1. Negative temperature coefficient "performance" for the PRF system at pressures of 40, 20, 10 and 5 bar, covering the temperature range of 650 K < T < 1200 K. Experimental data from Fieweger *et al.* (1997)

Figure 2 shows the numerical response for *n*-heptane / air mixtures at different pressures and compositions. The predictions are then compared to experimental data available in the literature Zhang *et al.* (2016)). It can be observed that

the NTC behavior induced by the linear chain c-c carbon structure remains for lean, stoichiometric, and rich mixtures. The oxidation of n-heptane has been widely studied, it is representative of a normal alkane. It is also a component in the composition of toluene as a reference fuel, a replacement representation for gasoline in research on combustion processes for internal combustion engines (ZHANG et al, 2016). The IDT simulations for the n-heptane/air mixture for different pressure conditions, in the temperature range from 800 to 1200 K, at stoichiometry, are presented in Figure 2. The reduction in reactivity causes the IDT to rise again at low temperatures, in this case, the effect of NTC, which makes sense as it mainly affects straight-chain hydrocarbons. A competition between the peroxide formation reactions and how their less reactive products, such as alkenes or cyclic ethers, is one of the factors responsible for the drop in the reactivity of alkanes as the level of branching of the molecule increases. Reactivity, in turn, increases the length of linear chains. The great pressure of pressure in the ignition delay is also observed. Increasing the pressure increases the reactivity of the mixture, but even with this effect, the effect of NTC is observed in the intermediate temperature region, approximately 800 to 950 K.

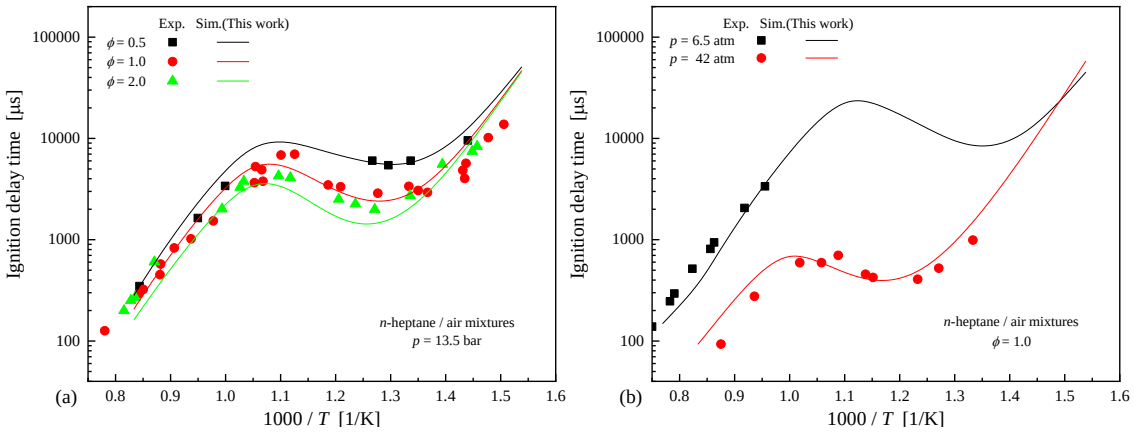

Figure 2. Negative temperature coefficient "performance" for the *n*-heptane system at pressures of 6.5 atm, 13.5 atm and 42 atm, lean, stoichiometric and rich composition, covering the temperature range of 650 K < T < 1200 K. Experimental data from Zhang *et al.* (2016)

4.2 Multicomponent gasoline surrogate mixtures

Figure 3 shows the numerical response of the detailed kinetics model of Ranzi *et al.* (2012). Data at 10 bar, 30 bar, and 50 bar and stoichiometric conditions. By the figure analysis, it can be observed that in the region that presents 20% of *n*-heptane at a pressure of 50 bar, for all temperatures there was an increase in the ignition delay with the increase in temperature, which indicates the presence of the region of NTC. For a pressure of 10 bar in mixtures A, B, C and D it is not possible to show the NTC region. The high concentration of unsaturated components suppresses the NTC behavior that can be mainly conferred by the presence of toluene. The suppression of NTC behavior by toluene is evident in the graphs where *n*-heptane fuel is present in different mixtures. When these fuel components are mixed, they reduce low-temperature reactivity.

The results obtained for the IDT as a function of 1000 K/T are shown in Figure 3 for the combustion of substitutes varying the percentage for *n*-heptane. Analyzing Figure 3, it is identified that when increasing the temperature, the IDT decreases, up to a temperature of 825K, for all mixtures with a concentration of 22% *n*-heptane and 50 bar. Where the NTC region is identified, with the increase in the IDT as a function of the increase in temperature. The NTC region occurs, for the conditions analyzed, for temperatures between 825K and 900K. From 900K onwards, the expected behavior is verified again, that is, a reduction in the IDT with an increase in temperature.

The IDT was determined through the largest peak of the OH* radical, when more than one peak of OH* is verified in the simulation, the program informs that there may be a cold flame, pre-ignition, or NTC behavior. In this sense, for all temperatures lower than 1000K, more than one peak of OH* was detected.

Figure 4 shows the numerical response for *n*-heptane/air mixtures and compositions concerning RON, MON, and the sensitivity analysis. It can be observed that as the percentage of *n*-heptane increases, there is a reduction in RON and MON. Based on the results obtained, through the sensitivity analysis it was observed the effect of the percentage of *n*-heptane on the magnitude of the affected reactions is captured, and in this case, as the percentage of *n*-heptane, that of RON and MON decrease. One of the parameters for the evaluation of fuels to work with high compression engines is the presence of the negative temperature coefficient and its characteristics since certain properties are directly linked to the concept of NTC as Motor Octane Number (MON) and Research Octane Number (RON). Thus, fuels that do not have the behavior of NTC are the most promising in this case. The brute force sensitivity analysis evaluates its effect on

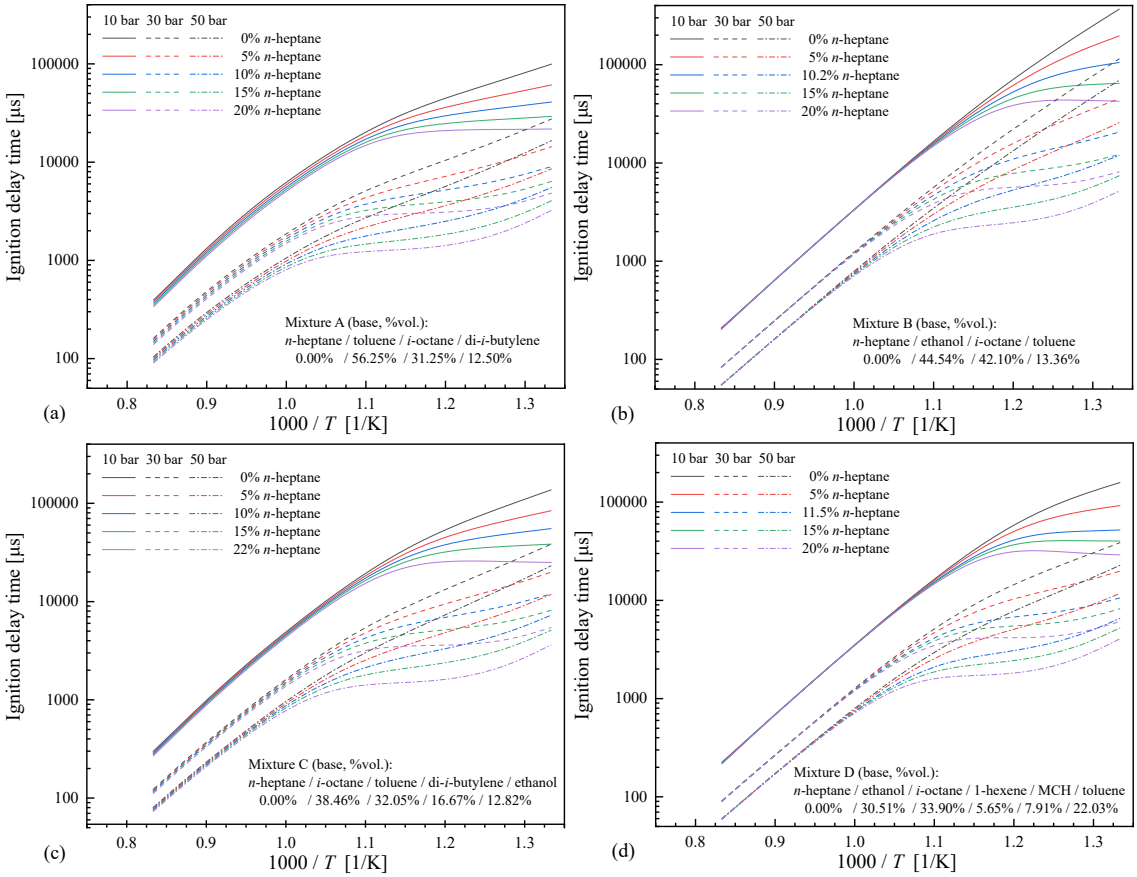

Figure 3. Numerical ignition delay time behavior for the multicomponent gasoline surrogate mixtures investigated in this work. (a) Mixture A, (b) Mixture B, (c) Mixture C and (d) Mixture D.

each reaction individually and evaluates its effect on flame velocity, and undisturbed turbulence, and then the sensitivity of each reaction individually. Normalized sensitivity analysis is the first-order analysis. This type of analysis becomes a very useful tool in evaluating and improving the mechanisms of chemical kinetics. Because this improvement can be made when each reaction is evaluated and its Arrhenius parameters are evaluated.

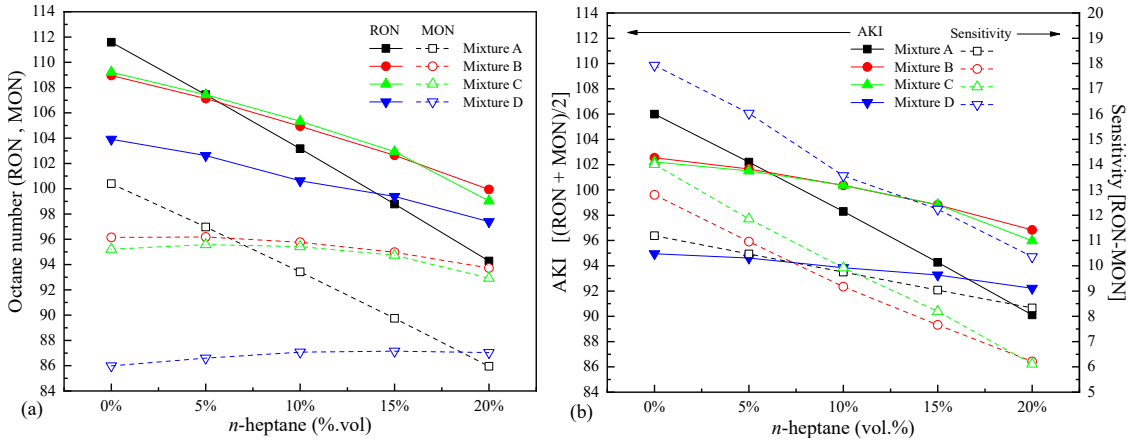

Figure 4. Numerical predictions of octane numbers of multicomponent gasoline surrogate mixtures investigated in this work. (a) Mixture A, (b) Mixture B, (c) Mixture C and (d) Mixture D.

5. CONCLUSION

In this work, a numerical evaluation of the influence of normal paraffin's on the fuel substitute formulation was performed. As gasoline substitutes, they were defined, simulated, and compared with experimental results available in the literature. The influence of the *n*-heptane percentage in the mixture was analyzed in terms of negative temperature

coefficient (NTC), the ignition delay times (IDTs) were simulated for four blends A, B, C, and D. The gasoline substitute blends were simulated using Cantera suit tools. As conclusions, it can be seen that in the region of temperature increase between 850 and 925 K there is an increase in the ignition delay, which results in a decrease in the average speed of the reactions. This is characterized as the negative temperature coefficient responsible for reducing the global net reaction rate with increasing temperature. It can be seen that the ignition delay, in the temperature range, has a maximum point just after 925 K, it decreases with increasing temperature, it has a minimum point just after the temperature of 1150 K. The proposed model reproduces the trend of experimental data for all mixtures investigated in this work, including pressure dependence. The results obtained will help to better understand the effects of mixing hydrocarbons, and serve as a basis for the development of fuel combustion for internal combustion engines.

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