



encit 2020



18th Brazilian Congress of Thermal Sciences and Engineering
November 16–20, 2020 (Online)

ENC-2020-0512

i-PENTANE AND *i*-PENTENE AS GASOLINE SURROGATES FOR THE TRANSPORT INDUSTRY: A NUMERICAL ANALYSIS ON IGNITION DELAY TIMES USING DETAILED CHEMICAL KINETICS

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Abstract. *Chemical kinetics of fuel surrogates is a very important topic under continuously development for improvements in internal combustion engines used in the transport industry sector. In this work, two chain branched chemical species, one saturated (*i*-Pentane) and other non-saturated (*i*-Pentene) were chosen for analysis. Ignition delay time data available at literature was then collected and used for assessment of a detailed kinetics model also available at literature. For *i*-Pentane the experimental data cover the temperatures from $1000\text{K} < T < 1550\text{K}$, pressures of 1.22, 9.76 and 24.78 bar and stoichiometries of $\phi = 0.3, 0.5, 1.0$ and 2.0 in air. For *i*-Pentene the experimental data cover the temperatures from $1330\text{K} < T < 1730\text{K}$, pressures of 1.75, 11.30 and 31.65 bar and stoichiometries of $\phi = 0.5, 1.0$ and 2.0 in oxygen and 99% argon diluted. The detailed kinetics model used for numerical simulation was validated against ignition delay times measurements of *n*-pentane, *i*-pentane, and neo-pentane (2,2-dimethylpropane) mixtures in shock tube and rapid compression machine. The model allows 3057 elementary reactions among 699 chemical species. Numerical simulations assuming constant volume reactor and brute force sensitivity analyses were then performed in order to understand the difference of numerical to experimental data. Simulation were performed using an open-source chemical kinetics software available at literature. The main sensitive reactions were then identified elucidating of this form the more important reactions plausible of optimization in order to reduce the error in numerical predictions.*

Keywords: *Gasoline surrogates, Detailed chemical kinetics, Ignition delay times, Brute force sensitivity analysis*

1. INTRODUCTION

Transport is almost entirely powered by internal combustion engines (ICEs) using petroleum-derived liquid fuels, additionally the global demand for transportation services is large and continuously increasing (Kalghatgi, 2018). Technology related to ICEs is always in evolution, new rules of emissions combined with the market competitiveness creates new opportunities for development and innovation. The focus of development in internal combustion engines (ICEs) is shifting toward improving fuel economy. Then knock caused by the autoignition of the fuel/air mixture ahead of the advancing flame front, is a major constraint on fuel efficiency of spark-ignition internal combustion engines (SI-ICEs), (Herzler *et al.*, 2007). All things considered understanding the chemistry behind this phenomenon is a barrier in coming up with new solutions. In order to better understand the chemistry of combustion process in ICEs, experimental and numerical strategies can be used. In this light numerical approaches several methodologies are available, from zero di-

mensional models involving simplified procedures till computational reactive fluid dynamics (CRFD) methodologies that involves very complex models for all the phenomenology present in the process (Merker *et al.*, 2012). The difference in terms of computational resources demand of each methodology can make the chosen numerical approach prohibitive (Cancino, 2009). Provided that the reaction rate term of the chosen combustion model also plays an important role, because it can also limit the numerical procedures in function of its computational resource demand. Usually, that term can be determined in several forms, which can be grouped as (a) global models, (b) semi-detailed models and, (c) detailed models, all of them defining the kinetics model to be used in the simulation. Above all the kinetics model is one of the more important parameters and, depending on the research focus or target, it should be necessary to use (or not) a detailed kinetics model. For ICEs research and looking at the engine performance assessed by emissions and knocking it is very common to use zero-dimensional models combined with detailed chemical kinetics models for the reaction rate. To that end detailed kinetics models serve as a useful tool to evaluate engine-relevant behavior, ignition properties, and pollutant formation (Ye *et al.*, 2018). From this numerical point of view, it is common to define a surrogate mixture of chemical species with the advantage of performing analysis with the characterization of a reduced number of chemical species when compared to the complexity of a real fuel. This strategy has been used systematically by many research groups around the world (Cancino *et al.* (2011); Andrae (2011); Metcalfe *et al.* (2007) and references therein). Chromatographic data analysis reveals that real gasoline for SI-ICEs usually contain chemical species with carbon atoms from C5 to C8 (Piehl *et al.*, 2018; Cancino, 2009), it means that species choose as gasoline surrogates could have 5 to 8 carbons atoms. The higher the molecular weight of fuel the higher the number of elementary reactions and chemical species involved in the kinetics model, of this form, it is very common to find big detailed kinetics models in the literature involving hundreds of chemical species among thousand elementary reactions, as for example the kinetics model for pyrolysis, partial oxidation and combustion of hydrocarbons and oxygenated fuels developed by the CRECK Modeling Group, which has a total of 484 species among 19341 reactions (Ranzi *et al.*, 2012). Branched paraffin as *i*-pentane are present in real fuels and contribute to decreased knock tendency because of the side chains, especially when the methyl groups (CH_3) are found in the second from the end or center position of the basic carbon chain. Olefins as *i*-pentene shows higher values of octane sensitivity (RON - MON) preventing the autoignition and improving the fuel quality. In this work, *i*-pentane and *i*-pentene, two potential chemical species identified in the literature as important components in determining the octane sensitivity of the fuel, an important trait for spark ignition engines (Piehl *et al.*, 2018) are numerically analyzed. In order to do it, the detailed kinetics model from Bugler *et al.* (2016) was used.

2. GASOLINE SURROGATES FOR THE TRANSPORT INDUSTRY

2.1 Real fuels vrs. Surrogate fuels - Species chemical groups of real fuels

The species number present in real gasoline can be in the hundreds, involving saturated and unsaturated hydrocarbons, including alkanes, cycloalkanes, alkenes, cycloalkenes, aromatics, and other components whose identity and quantities are usually unknown (Metcalfe *et al.*, 2007; Cancino *et al.*, 2009b; Curran *et al.*, 1998). Not only the gasoline composition can vary widely depending on the origin of the crude oil and the refining process. But also, the high chemical and physical complexity of a fuel is directly related to the high number of substances that are present. Yet for research purpose, in order to reduce complexity and still maintaining the physical and chemical characteristics, such as ignition delay time, burning velocity, viscosity, vaporization and emissions, the practical fuel can be represented by a simple mixture of a reduced number of pure substances, which is known as a fuel surrogate (da Silva Jr. *et al.*, 2019). Table 1 from Piehl *et al.* (2018) shows the chromatographic data analysis of the well-known research grade gasoline (RD387), in which is possible to identify five species chemical groups: (a) *n*-alkanes, (b) *i*-alkanes, (c) olefins, (d) naphthenes and (e) aromatics. Please note that small portions of species in this fuel are non-classified species.

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

C#	<i>n</i> -alkanes	<i>i</i> -alkanes	olefins	naphthenes	aromatics	not classified	total per carbon
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 Table 1 can be identified that for the RD378 sample analyzed, *n*-alkanes (C_nH_{2n+2}) represent quite 10% of the

volumetric composition being the 4.36% species with seven carbons atoms ($n\text{-C}_7\text{H}_{16} \Rightarrow n\text{-heptane}$). In commercial gasoline n -alkanes usually range from n -butane to n -dodecane. In terms of ignition delay time (IDT), the general trend observed, is that a decrease in IDT occurs by increasing the carbon chain length (Piehl *et al.*, 2018). The n -alkanes content in the fuel will impact the IDT behaviour of the mixture, the higher the vol.% of n -alkanes, the higher the negative coefficient temperature behavior in the fuel (Cancino *et al.*, 2011). Chain branched alkanes (i -alkanes) is the largest of the major hydrocarbon groups found in the RD378 sample, covering 42.25% as can be seen in Table 1). Also, it is possible to observe that i -alkanes with 6, 7 and 8 carbons atoms ($i\text{-C}_8\text{H}_{18} \Rightarrow i\text{-octane}$, for example) represent more than 90% of that chemical group in the RD378 gasoline. Additionally, the i -alkanes content in the fuel will impact the IDT behaviour of the mixture, the higher the vol.% of i -alkanes, the lower the negative coefficient temperature behavior in the fuel (Cancino *et al.*, 2011). Importantly n -heptane and i -octane are the primary reference fuels used to define the Research Octane Numbers of practical fuels. Olefins, also known as alkenes, compose a large of transportation fuels such as gasoline, diesel, and aviation fuel. For example, gasoline consists of 15-20% olefins by volume (Westbrook *et al.*, 2015). Olefins are hydrocarbon compounds with one or more carbon double bonds and are normally present in gasoline in small quantities, in the case of the RD378 sample of Table 1, the content is 4.7% (vol.%). One double bond has little antiknock effect, while the presence of two or three bonds considerably increases the antiknock effect (Heywood, 1988). Because of their chemical structure, olefins can increase the reactivity of gasoline as well as improve its octane number. Smaller, branched olefins such as i -Pentene (2-methyl,2-Butene) are well-known to exhibit strong octane sensitivity, with fairly high research octane number (RON) but much smaller motor octane number (MON). The RON and MON for i -pentene are 97.3 and 84.7, respectively (Lovell, 1948), and this variation persists to olefin species as large as 2,4,4-trimethyl-1-pentene (C_8H_{16}) with RON greater than 100 and MON of 86.5. Likewise, Leppard (1990) has discussed these octane sensitivities quite thoroughly and attributes them to a lack of low-temperature reactivity in these olefins, since these sensitive fuels produce little or no negative temperature coefficient (NTC) behavior or low-temperature reactivity (Westbrook *et al.*, 2015). Naphthenes or Cycloalkanes are saturated hydrocarbons that contain one or more rings, each of which may have one or more paraffin side chain. Cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbons atoms that make up the ring are single bonded to other atoms. They constitute a significant portion of conventional diesel, jet fuel, and gasoline, reaching up to 35%, 20%, and 15% by volume, respectively (Pitz *et al.*, 2007).

2.2 Typical fuel surrogates used for combustion research

The analysis of the combustion process focused on ICEs shows that many research groups around the world have been used and proposed several chemical species as gasoline surrogate potential candidates for research purposes. A big quantity of published literature (Andrae (2011); Cancino *et al.* (2009b); Pitz *et al.* (2007); Ranzi *et al.* (2012); Cheng *et al.* (2017); Tian *et al.* (2011); Curran *et al.* (2002); Metcalfe *et al.* (2007) and references therein) support this fact. Provided this Table 2 shows some of the more common chemical species used by different groups for research purposes.

Table 2. Chemical compounds used 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	24.80	26.00	-1.20
n -Pentane	Pentane	n -Paraffin	C_5H_{12}	72.15	61.70	62.60	-0.90
i -Octane	2,2,4-trimethyl-Pentane	i -Paraffin	C_8H_{18}	114.23	100.00	100.00	0.00
n -Heptane	Heptane	n -Paraffin	C_7H_{16}	100.20	0.00	0.00	0.00
i -Pentane	2-methyl,Butane	i -Paraffin	C_5H_{12}	72.15	92.30	90.30	2.00
m -Xylene	1,3-dimethyl-Benzene	Aromatic	C_8H_{10}	106.17	117.50	115.00	2.50
Methylcyclohexane	MCH	Naphthene	C_7H_{14}	98.19	74.80	71.10	3.70
Cyclohexane	Hexanaphthene	Naphthene	C_6H_{12}	84.15	83.00	77.20	5.80
i -Pentene	2-methyl,2-Butene	Olefin	C_5H_{10}	70.13	97.30	84.70	12.60
Mesitylene	1,3,5-trimethyl-Benzene	Aromatic	C_9H_{12}	120.19	120.30	106.00	14.30
1-Hexene	1- n -Hexene	n - α -Olefin	C_6H_{12}	84.16	76.40	63.40	13.00
Toluene	methyl-Benzene	Aromatic	C_7H_8	92.14	120.10	103.50	16.60
Di-iso-butylene(2)	2,4,4-trimethyl-2-Pentene	Olefin	C_8H_{16}	112.21	103.50	86.20	17.30
Di-iso-butylene(1)	2,4,4-trimethyl-1-Pentene	Olefin	C_8H_{16}	112.21	106.00	86.50	19.50

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

From Table 2 it is possible to see the big options span related to the different properties, some chemical species shown low or negative sensitivities indicating a tendency to low IDTs and of this form knock tendency. Other chemical species shows high sensitivities, as Di-iso-butylene(1) (2,4,4-trimethyl-1-Pentene). Note that all of them are used and investigated because of the different physic-chemical properties. Meaning that when mixed in the right proportion they will return a gasoline surrogate mixture with physical, chemical, thermodynamic and combustion properties close to the ones of the real (practical) target fuel. Thus making the research process feasible. To give an illustration Table 3 lists several detailed kinetics databases for gasoline surrogates. It is possible to identify the number of chemical reactions, the

number of of chemical species as well as the validation method used for each kinetics model. Notably some of them are multi-component detailed kinetics models.

Table 3. Kinetics databases available in the literature for gasoline surrogates

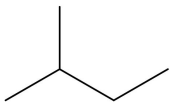
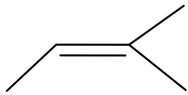
Author	Surrogates	Reactions	Species	Validation
Westbrook <i>et al.</i> (2009)	<i>n</i> -heptane, <i>i</i> -octane	8157	2115	P, ST, FR, JRS
Silke <i>et al.</i> (2007)	Cyclohexane	4269	1081	RCM, JSR
Curran <i>et al.</i> (1998)	<i>n</i> -heptane, <i>i</i> -octane	4236	1034	HPFR
Cancino <i>et al.</i> (2009b)	<i>n</i> -heptane, <i>i</i> -octane, toluene, ethanol	4743	1056	HPST
Cancino <i>et al.</i> (2009a)	<i>i</i> -octane, ethanol	4743	1056	HPST
Metcalfe <i>et al.</i> (2007)	Di-iso-butylene	3783	897	HPST
Curran <i>et al.</i> (2002)	<i>i</i> -octane	3606	857	ST, RCM, JSR
Gudiyella <i>et al.</i> (2011)	<i>m</i> -xylene (1,3-dimethyl-Benzene)	1158	174	ST
Cancino <i>et al.</i> (2011)	<i>n</i> -heptane, <i>i</i> -octane, toluene, ethanol, Di-iso-butylene	4959	1126	HPST
Andrae (2011)	Low alkylbenzenes	767	150	ST, JSR
Tian <i>et al.</i> (2011)	toluene	1740	273	LFS, JSR
Bugler <i>et al.</i> (2016)	pentane isomers	3057	699	HPST, JSR
Cheng <i>et al.</i> (2017)	<i>i</i> -pentene	3228	698	LFS

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

2.3 *i*-Pentane and *i*-Pentene

In this work, two chain-branched chemical species, one saturated (*i*-Pentane), and one non-saturated (*i*-Pentene) were chosen among the palette of chemical species listed in Table 2. While models for normal chain alkanes have been developed over the last decades, little work has been performed on branched alkanes, which are a widely used in petrol and diesel fuels (Bugler *et al.*, 2016). Among the alkenes, pentene takes the largest proportion, accounting for about 8.04% in Chinese gasoline (Cheng *et al.*, 2017). That said Table 4 shows the main properties of both chemical species.

Table 4. Main properties of *i*-Pentane and *i*-Pentene

Species	Other names	Chemical structure	Formula	Molecular weight	RON ^a	MON ^a
<i>i</i> -Pentane	2-methyl-Butane		C ₅ H ₁₂	72.14	92.30	90.30
	1,1,2-Trimethylethane					
	2-methyl-Butane					
	<i>i</i> -C ₅ H ₁₂					
	ethyl-dimethyl-Methane					
	<i>i</i> -Amylhydride					
	Exxsol <i>i</i> -Pentane S					
1,1-dimethyl-Propane						
<i>i</i> -Pentene	methyl-Butane		C ₅ H ₁₀	70.13	97.30	84.70
	2-methyl,2-Butene					
	trimethyl-Ethylene					
	β - <i>i</i> -Amylene					
	1,1,2-trimethyl-Ethylene					
	2-methyl-2-Butene					
	3-methyl-2-Butene					
2-Methylbut-2-ene						
<i>n</i> -Amylene						
Ethylene, trimethyl-						

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

The main target in this work is to understand the kinetics process of both the chemical species and assess the numerical performance of detailed kinetics models available at the literature (Bugler *et al.*, 2016) used to predict ignition delay times obtained in shock tubes at engine-like-conditions of temperature, pressure, and stoichiometry. Experimental data of IDTs was also obtained from the literature (Bugler *et al.*, 2016; Westbrook *et al.*, 2015)

3. METHODOLOGY

3.1 The detailed kinetics model used in this work

The detailed kinetics model from Bugler *et al.* (2016) was used for numerical simulation. The model was developed at the Combustion Chemistry Centre and validated against IDT of *n*-pentane, *i*-pentane, and *neo*-pentane (2,2-dimethyl-Propane) mixtures that were measured in two shock tubes and a rapid compression machine. The model allows 3057

elementary reactions among 699 chemical species. After an exhaustive literature review, the chosen model from Bugler *et al.* (2016) was the unique model with both the species incorporated in the list of species. Other models were reviewed, however, only one of both was found in the list of species.

3.2 Shock tube experimental data for *i*-Pentane and *i*-Pentene available at the literature

In this work, the experimental data from Bugler *et al.* (2016) from *i*-Pentane and data from Westbrook *et al.* (2015) from *i*-Pentene were used to numerically assess the detailed kinetics model from Bugler *et al.* (2016). For *i*-Pentane the experimental data cover the temperatures from $1000\text{K} < T < 1550\text{K}$, pressures of 1.22, 9.76 and 24.78 bar and stoichiometries of $\phi = 0.3, 0.5, 1.0$ and 2.0 in air. For *i*-Pentene the experimental data cover the temperatures from $1330\text{K} < T < 1730\text{K}$, pressures of 1.75, 11.30 and 31.65 bar and stoichiometries of $\phi = 0.5, 1.0$ and 2.0 in oxygen and 99% argon diluted.

3.3 The in-house computational tools for analysis

Two Python scripts native to CANTERA (Goodwin *et al.*, 2018) were adapted for the research purposes of this work. The first one simulated the kinetics behavior of a reactive system assuming constant volume condition. The details of the experimental methodology for IDT determination are presented at Bugler *et al.* (2016) for *i*-Pentane and at Westbrook *et al.* (2015) for *i*-Pentene. However, it's important to attend to the details on how each experiment determines the ignition delay time, the most usual is to define the time between the arrival of the shock wave in the end-wall 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's a well accepted practice. Nevertheless for diluted mixtures the definition changes and the ignition delay time corresponds to the time between the passage of the reflected shock wave and the intersection of lines drawn along the steepest rate-of-change of OH* de-excitation and a horizontal line which defines zero-concentration level (as can be seen in figure 5 from Bugler *et al.* (2016) and figure 1b from Westbrook *et al.* (2015)). For detailed chemical kinetics analysis, the brute force sensitivity analysis methodology was used. Equation 1 shows the sensitivity criteria adopted in this work for the brute force analysis.

$$S_{(\text{sensitivity})} = \frac{\tau_{\text{with perturbation}}}{\tau_{\text{without perturbation}}} - 1 \quad (1)$$

Therefore, if the sensitivity (S) is zero, the perturbed reaction has no influence on IDT, if the sensitivity (S) is higher than zero, the perturbed reaction increases the IDT (positive influence) and conversely it reduces the IDT (negative influence). Reactions with sensitivities below the threshold (0.005) were then ignored for plotting. The brute force sensitivity analysis, programmed in CANTERA Goodwin *et al.* (2018) took 55.5 hours running in a HP - Workstation Intel Xeon E5420 CPU @ 2.50 GHz. The second Python script performs the brute force sensitivity analysis described here (Equation 1). Both the programs have been improved by the Vehicular Systems Energy Efficiency Research Group, of the Internal Combustion Engines Laboratory - LABMCI / CTJ / UFSC in a collaborative effort by different users and researchers of the group.

4. RESULTS AND DISCUSSION

4.1 Ignition delay time predictions

All the numerical predictions for both the species investigated in this work and the experimental measurements from literature are plotted in Figure 1. It is noticeable that for *i*-Pentane /air mixtures (Figures 1 (a), (b) and (c)) in all the experimental conditions the behavior of the kinetics model used in this work is more accurate when compared to the *i*-Pentene / O₂ 99% argon diluted mixtures numerical to experimental comparison (Figures 1 (d), (e) and (f)). Note that for each species the scales (IDT and $1000/T$) of figures were keep identical in order to visualize and compare the effect on pressure and composition (ϕ). The kinetics model shows good behavior for higher pressures specially for all compositions (ϕ), Figures 1(c) When decreasing pressure, the trend of experiments is the same however the prediction became poor, particularly for leaner mixtures ($\phi = 0.3$). Another important observation from experimental data is that for pressure $p = 9.76$ bar, there is no noticeable IDT data span with the composition (ϕ), Figure 1(b), in other words, all the data shows the typical trend increasing the IDT when the temperature decreases for all stoichiometries and with similar values of IDT. For low pressures ($p = 1.22$ bar, Figure 1(a)) and high pressures ($p = 24.78$ bar, Figure 1(c)) the difference of IDT based on ϕ is clear, the detailed kinetics model follows that behaviors. Also, note that for *i*-Pentane, there is a pressure / stoichiometry inverted behavior on IDT, it means, for high pressures leaner mixtures hold the high IDT values, for low pressures, leaner mixtures hold the low values of IDT. For *i*-Pentene (Figures 1 (d), (e) and (f)) normal behavior of IDT on pressure, temperature and composition are then observed for experimental data; IDT increasing as the mixture enriches for all pressures and temperatures. Concerning to the numerical predictions, it is clear that the model is able to reproduce

the overall trend of experiments, however, the numerical prediction is very poor for low pressures ($p = 1.75$ bar, Figure 1(d)) and discretely improved for high pressures ($p = 31.65$ bar) and rich mixtures ($\phi = 2.0$), Figure 1(f).

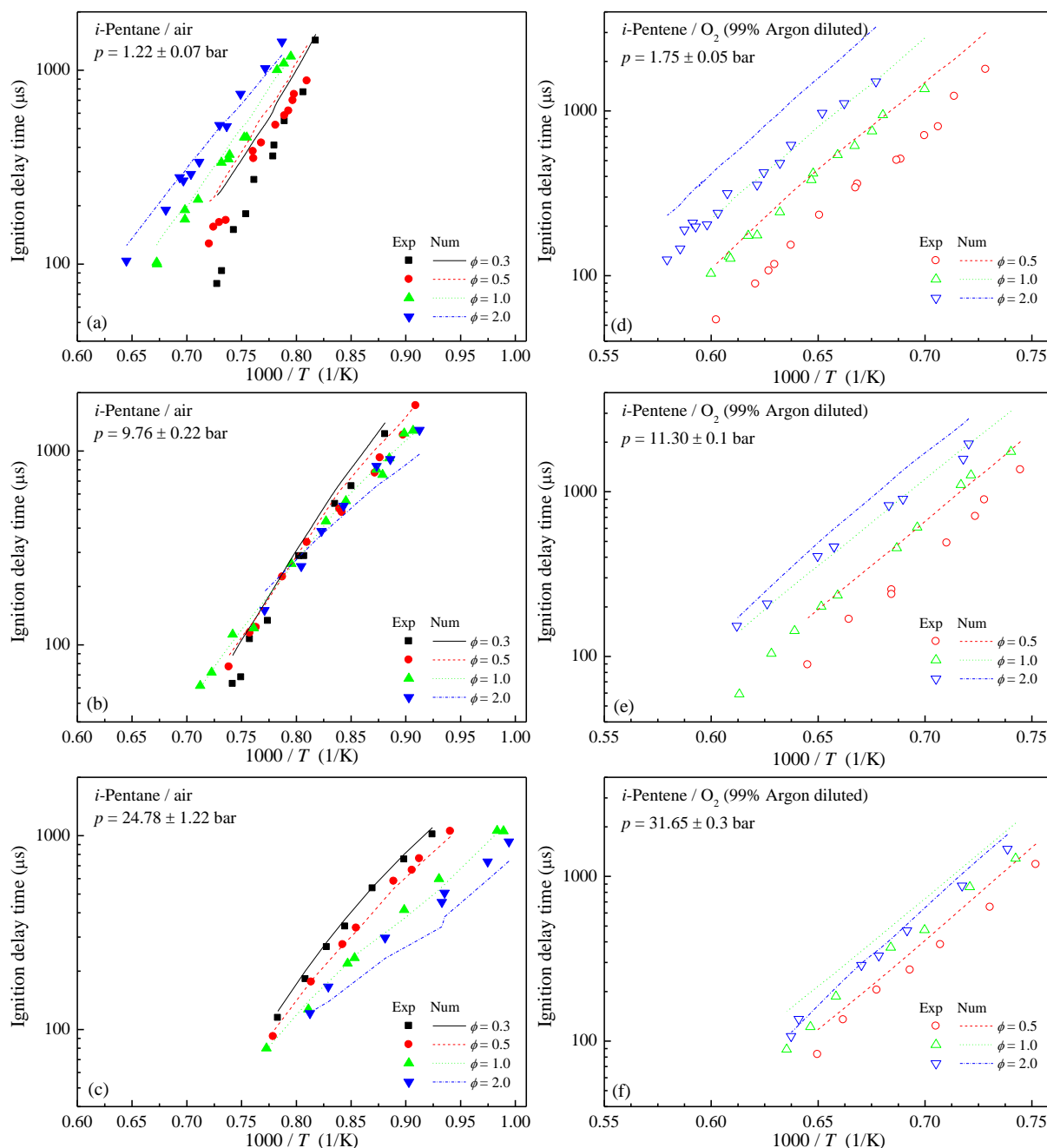


Figure 1. (a), (b) and (c) *i*-Pentane /air mixtures, experimental data from Bugler *et al.* (2016). (d), (e) and (f) *i*-Pentene / O_2 99% argon diluted mixtures, experimental data from Westbrook *et al.* (2015)

4.2 Brute force sensitivity analysis

In order to better understand the numerical vs experimental differences, intended as a fault in the detailed kinetics model, a brute force sensitivity analysis was performed. Sensitivity analyses are performed to identify the most important reactions controlling the desired prediction like the IDT and / or flame speed. Brute force sensitivity analysis involves increasing and decreasing each reaction rate expression by a factor and calculating the effect on the predicted factor, IDT for example (Metcalf *et al.*, 2013). Because of the big differences among experimental to numerical data of *i*-Pentene, simulations were performed for eighteen sets of conditions: temperatures of 1400 K and 1550 K, stoichiometries were set at $\phi = 0.5, 1.0$ and 2.0 and three points of pressures were analyzed (1.75, 11.3 and 31.65 bar), with the perturbation being

generated by multiplying the reaction rate (k) of each reaction of the kinetics model by 0.5 and 2.0, and then calculating the IDT for each perturbation. These values are hallmark of IDT brute force because they are in a good range. Meaning that they are not too low, where the coefficients would become too suppress thus keeping reactivity, or too high. In total thirty-six simulations were then performed spending around two thousand hours of computation / simulation process, that time of computation was covered in an 8-core HP - Workstation Intel Xeon E5420 CPU @ 2.50 GHz, using six cores simultaneously resulting in 26 days - full time - calculation. Figures 2 and 3 shows the results for perturbation $k = 0.5$ and $k = 2.0$ respectively.

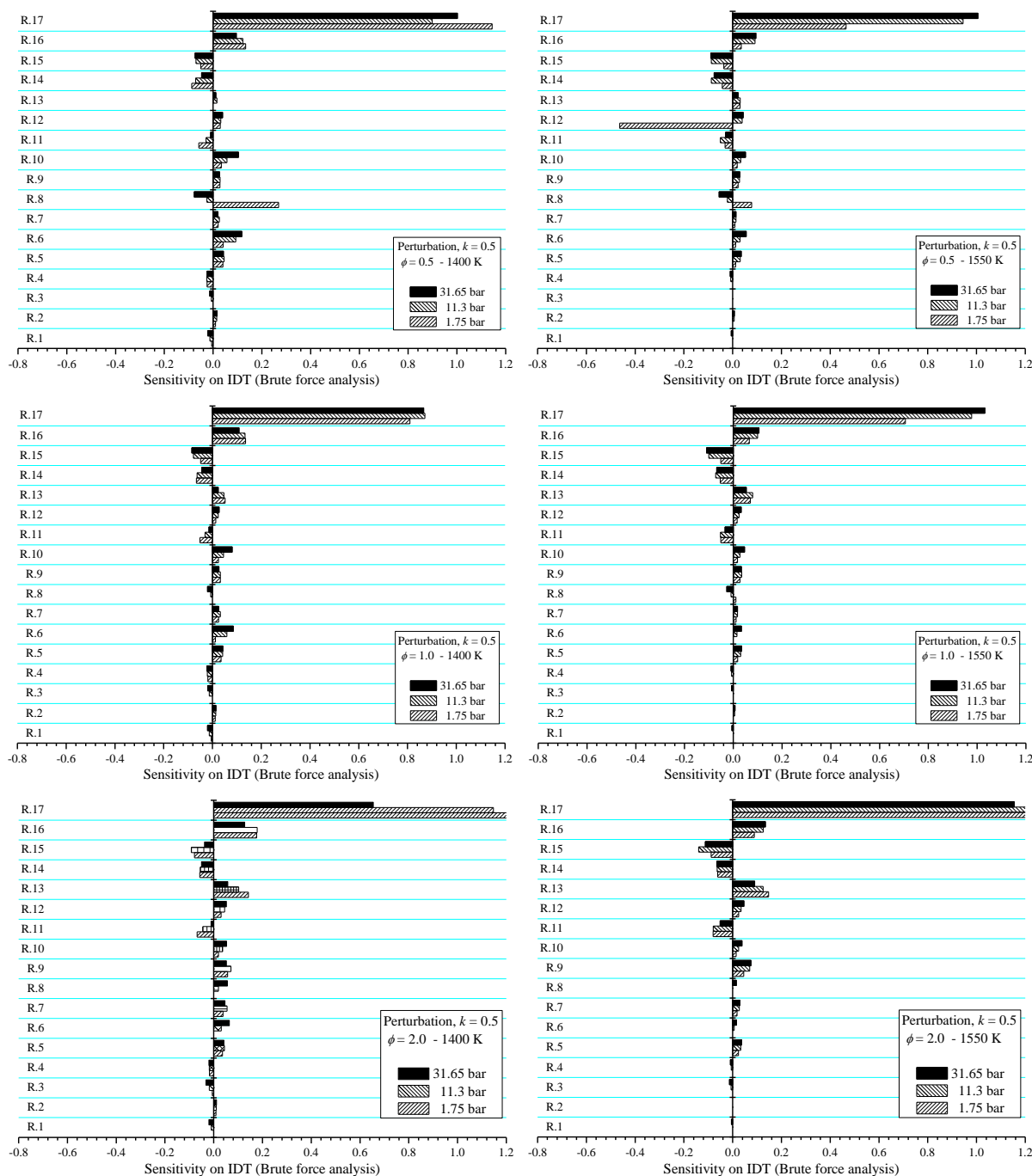


Figure 2. Brute force sensitivity on IDT for *i*-Pentene/O₂ (99% Argon diluted) mixtures at pressures of 31.62, 11.3 and 1.75 bar, temperatures of 1400 K and 1550 K and composition (ϕ) of 0.5, 1.0 and 2.0. Perturbation of $k \times 0.5$

The output files of all simulations were then manually post-processed and seventeen reactions, listed below, were found in common for all the sensitive conditions as the more important when the perturbation (k) returns representative variation on IDT for that reaction. As expected, reactions of the H₂/O₂ system are ranked in the sensitivity analysis, (R.17), (R.12) and (R.8). The Arrhenius parameters of these reactions have been well defined by many research groups

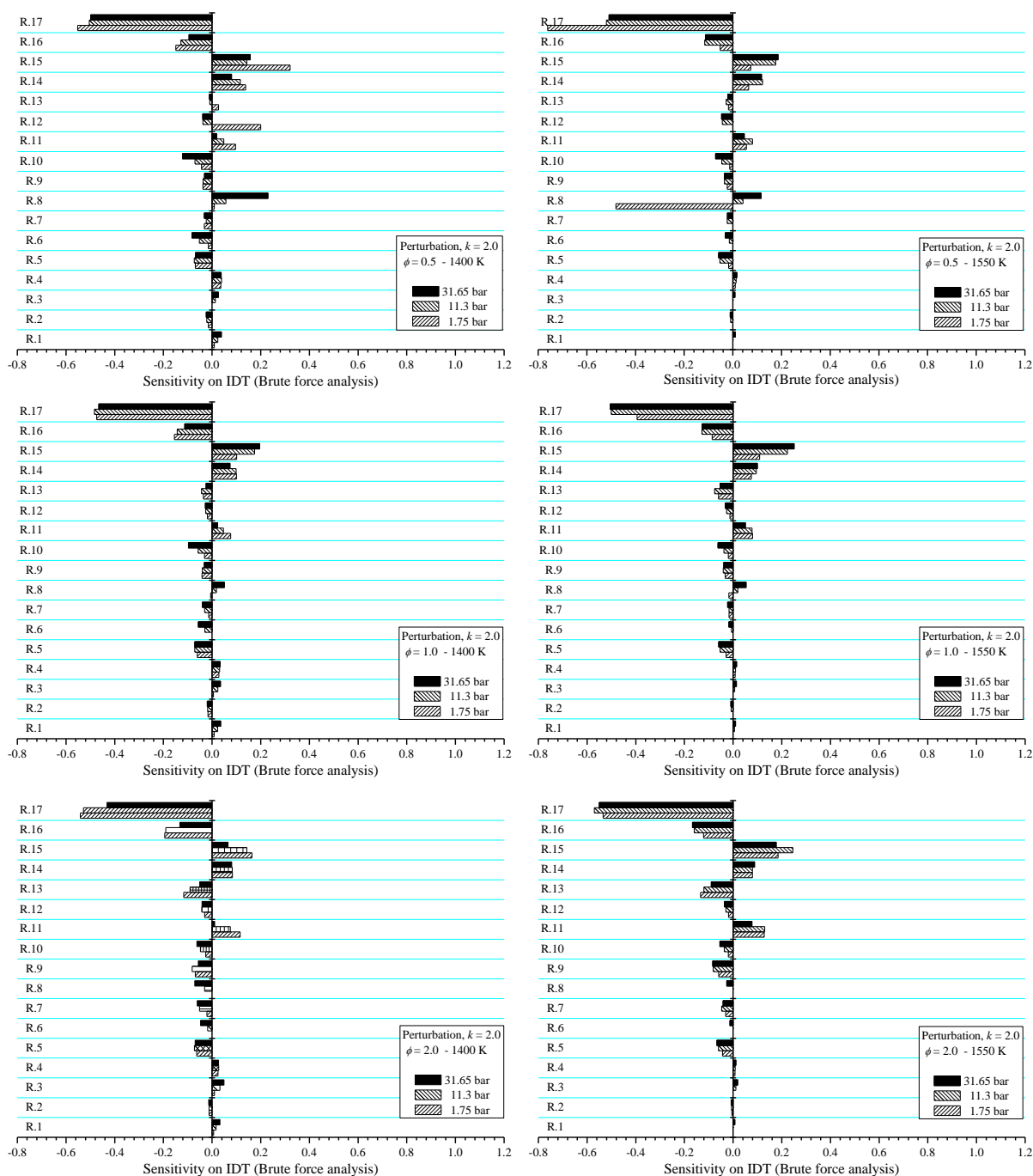
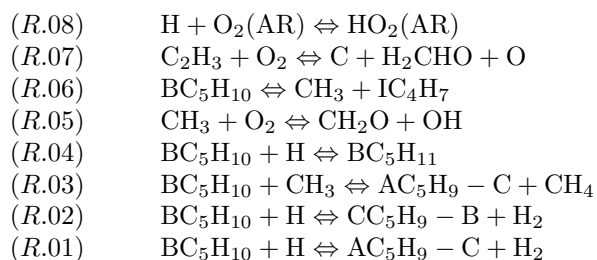
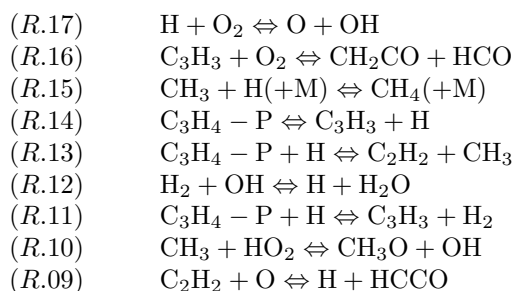


Figure 3. Brute force sensitivity on IDT for *i*-Pentene/ O_2 (99% Argon diluted) mixtures at pressures of 31.62, 11.3 and 1.75 bar, temperatures of 1400 K and 1550 K and composition (ϕ) of 0.5, 1.0 and 2.0. Perturbation of $k \times 2.0$

around the world. Reactions involving *i*-Pentene (R.6), (R.4), (R.3), (R.2) and (R.1) were pointed out by the brute force analysis as important.



To come to this selection the difference between the experimental IDT and the numerical was set as a goal value in each sensibility set of conditions, for example at 1550 K, $\phi = 0.5$ and 1.75 bar the numerical IDT is 61% higher than the experimental value. So, the process is to select the reactions that receiving the perturbation (k) decreases the IDT value in this range more than where the difference would be milder. From this group of sensitive reactions, two among them are potential elementary reaction for further kinetics model improvement, reaction $R.06$ involving radical methyl ($\dot{\text{C}}\text{H}_3$) abstraction from *i*-Pentene and reaction $R.04$ involving the opening of the double C=C bond and addition of hydrogen atom to the *i*-Pentene. There are other two elementary reactions, $R.16$ and $R.13$, not involving the *i*-Pentene directly, instead, involving sub-products of *i*-Pentene decomposition (C_3H_3 and C_3H_4), molecular oxygen (O_2) and hydrogen atoms (H).

5. CONCLUSION

In this work, two chain-branched chemical species, one saturated (*i*-Pentane), and one non-saturated (*i*-Pentene) were chosen for analysis. Shock tube data available at literature was used for assessment of a detailed kinetics model from Bugler *et al.* (2016). For *i*-Pentane the experimental data cover the temperatures from $1000\text{K} < T < 1550\text{K}$, pressures of 1.22, 9.76 and 24.78 bar and stoichiometries of $\phi = 0.3, 0.5, 1.0$ and 2.0 in air. For *i*-Pentene the experimental data cover the temperatures from $1330\text{K} < T < 1730\text{K}$, pressures of 1.75, 11.30 and 31.65 bar and stoichiometries of $\phi = 0.5, 1.0$ and 2.0 in oxygen and 99% argon diluted. All the experimental points for both the species investigated in this work were simulated by using in-house computational tools over open-source software available at literature (CANTERA, Goodwin *et al.* (2018)). Results indicate that the detailed kinetics model from Bugler *et al.* (2016) can reproduce the experimental trend for both the gasoline surrogates, however it over-predicts the IDT for *i*-Pentene when compared to experimental results. The detailed kinetics model can capture the pressure / stoichiometry inverted behavior on IDT over the experimental conditions tested in this work. A set of elementary reactions pointed out by the brute force sensitivity analysis as the more sensitive for *i*-Pentene thermal oxidation should be analyzed and revised in the kinetics model to adjust the numerical to the experimental data. The optimization process of these reactions could be performed using several methodologies available at literature, some of them involving computational chemistry. Additional validation process using laminar flame speed data and plug flow / jet stirred reactors are necessary to complement the validation of this kinetic model. The kinetics model also needs to be tested for intermediate to low temperatures ($T < 1000\text{K}$) to use it in numerical simulations at internal combustion engine-like conditions.

6. ACKNOWLEDGEMENTS

The authors like to acknowledge the UFSC Joinville TI team for all support given to the LABMCI computer network.

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