

## ISOCETANE ( $i\text{-C}_{16}\text{H}_{34}$ ), HEXADECANE ( $n\text{-C}_{16}\text{H}_{34}$ ) AND METHYL-CYCLOHEXANE ( $\text{C}_7\text{H}_{14}$ ) AS JET-FUEL SURROGATES: A NUMERICAL STUDY OF IGNITION DELAY TIME

Leonel R. Cancino, leonel@labcet.ufsc.br

Amir A.M. Oliveira, amir@emc.ufsc.br

Combustion and Thermal Systems Engineering Laboratory–LabCET  
 Dep. of Mechanical Engineering  
 Federal University of Santa Catarina  
 Brazil.

Edimilson Oliveira, edimil@petrobras.com.br

Mauro Iurk Rocha, miurk@petrobras.com.br

PETROBRAS/CENPES/PDAB/COMB  
 Av Horácio Macedo, 950  
 Cidade Universitária - Ilha do Fundão  
 21941-598 - Rio de Janeiro – RJ  
 Brazil.

**Abstract.** Aviation fuels (jet fuels) are composed by thousand of chemical species. In order to make numerical and experimental studies tractable it is necessary to propose chemical species as “fuel surrogates”; chemical species completely characterized, simplifying the analysis complexity and allowing simplified numerical and experimental approaches. This work presents a numerical study of the chemical kinetics of the ignition delay time for three complex hydrocarbons adopted as jet fuel surrogates: iso-cetane (2,2,4,4,6,8,8-heptamethylnonane,  $i\text{-C}_{16}\text{H}_{34}$ , branching chain alkane), hexadecane ( $n\text{-C}_{16}\text{H}_{34}$ , alkane) and methylcyclohexane ( $\text{C}_7\text{H}_{14}$ , cyclo-paraffin). The chemical kinetics is reviewed in terms of ignition delay time, by using CHEMKIN as computational tool, under gas turbines like conditions ( $600\text{ K} < T < 1200\text{ K}$ ,  $5\text{ bar} < p < 30\text{ bar}$ ), employing detailed kinetics models available at literature.

**Keywords:** Fuel research, Detailed chemical kinetics, Ignition delay time, Fuel surrogates

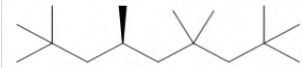
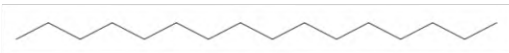
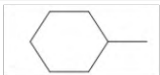
### 1. INTRODUCTION

Transportation fuels like jet fuels, diesel fuel and gasoline are typically complex distillate mixtures comprised of hundreds to thousands of hydrocarbon compounds, making impossible a detailed chemical kinetics approach. To deal with this complexity, species can be collected into basic structural classes in order to understand their combustion properties and construct surrogate mixtures for those practical fuels.

Those structural classes of compounds are usually  $n$ -alkanes, branched or  $i$ -alkanes, aromatics, polycyclic alkanes, olefins, naphthenes, and oxygenated hydrocarbons. Selecting one or two chemical species representing each basic structural classes, makes the numerical approach tractable. The structure of a hydrocarbon fuel has a profound impact on the ignition and other combustion properties of that fuel.

Chemical species like  $n$ -alkanes,  $i$ -alkanes and cyclic alkanes are important components in all of these practical transportation fuels. In this work, a numerical study of the chemical kinetics of three complex hydrocarbons adopted as jet fuel surrogates:  $i$ -cetane (2,2,4,4,6,8,8-heptamethylnonane,  $i\text{-C}_{16}\text{H}_{34}$ , branching chain alkane), hexadecane ( $n\text{-C}_{16}\text{H}_{34}$ , alkane) and methylcyclohexane ( $\text{C}_7\text{H}_{14}$ , cyclo-paraffin), is presented in terms of ignition delay time. Table 1 list the main characteristics of the fuel surrogates used in this work.

Table 1. Main characteristics of the fuels surrogates: (a)  $i$ -cetane, (b) hexadecane and (c) methylcyclohexane

	Molecular structure	Formula	Group	H/C Ratio	Molecular weight
(a)		$\text{C}_{16}\text{H}_{34}$	iso-paraffin	2.13	226.44
(b)		$\text{C}_{16}\text{H}_{34}$	n-paraffin	2.13	226.44
(c)		$\text{C}_7\text{H}_{14}$	cyclo-paraffin	2.00	98.18

L.R. Cancino, E. Oliveira, M.I. Rocha, A.A.M. Oliveira.

Isocetane, Hexadecane and Methyl-Cyclohexane as Jet-Fuel Surrogates: A Numerical Study of Ignition Delay Time.

The *i*-cetane (2,2,4,4,6,8,8-heptamethylnonane, *i*-C<sub>16</sub>H<sub>34</sub>) and hexadecane (highly branched alkane and linear alkane) are the reference compounds for determining cetane ratings. The *i*-cetane is also a candidate branched alkane representative in surrogate mixtures for diesel and jet fuels.

## 2. OXIDATION OF HYDROCARBONS - DETAILED KINETICS MODELS.

The oxidation of hydrocarbons proceeds either by hydrogen atom abstraction or by cleavage of C–C bonds at primary or secondary carbon atoms. In the case of aliphatic alcohol hydrocarbons, the hydroxyl group plays a very important role for the oxidation and as a third pathway the cleavage of the C–O bond can occur. Any of the three paths proceeds after a temperature activated perturbation of the energy field of the molecule and can proceed either intramolecular (isomerization) giving several sub-structures or as a result of collision with active radical species. Independently of the case, reaction mechanisms show several characteristic properties.

Usually, reaction mechanisms in combustion follow a chain process composed by initiation, propagation, branching and termination reactions. The oxidation of hydrocarbons also follows a chain process. Methane was the first hydrocarbon analyzed because of its simplicity. The first detailed kinetics model for high temperature oxidation of methane dealt with the methane reaction as an H-atom abstraction sequence from methane, forming methyl radical (CH<sub>3</sub>), with posterior conversion to formaldehyde (CH<sub>2</sub>O), and then to formyl radical (HCO) and carbon monoxide (CO) and finally oxidation to carbon dioxide (CO<sub>2</sub>).

This kinetics scheme for methane was discarded, because it was soon verified that CH<sub>3</sub> can recombine to ethane C<sub>2</sub>H<sub>6</sub> and finally form H<sub>2</sub>O and CO<sub>2</sub> (Westbrook et al., 2005). Afterward, a very important conclusion was obtained: A detailed kinetics model can be structured in a hierarchical form, taking as base the kinetics of small hydrocarbons and completing the kinetics model with additional reactions for the bigger chemical species. Figure 1 shows a schematic representation of the hierarchy of the kinetics model for hydrocarbons oxidation.

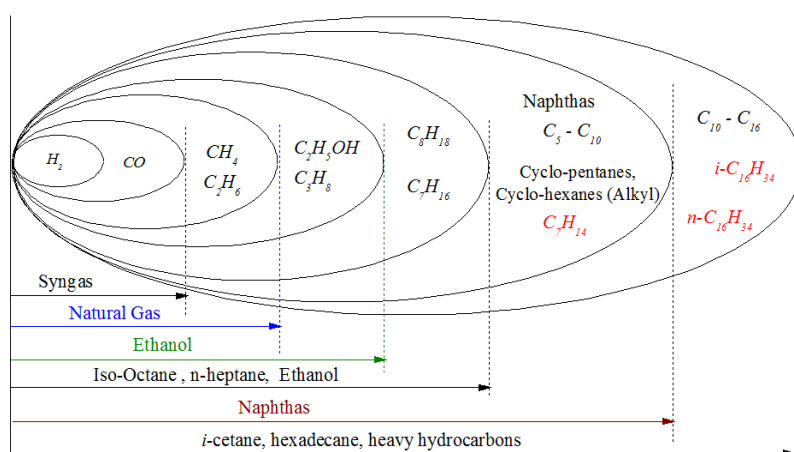


Figure 1. Hierarchy of kinetics models for hydrocarbons oxidation (adapted from Warnatz et al., 1999).

Detailed kinetics models provide more in-depth information into the time and spatial evolution of the concentration of chemical species in a combustion system.

A well structured detailed kinetics model must be able to describe all the stages of the kinetics process, beginning with the pyrolysis/thermal decomposition of the fuel, followed by the total or partial depletion of the fuel, formation and consumption of intermediate species and finally describing the formation of saturated combustion products. The detailed kinetics models used in this work are briefly described in the Table 2.

Table 2. Detailed kinetics models used in this work.

Kinetics model	Elements	Chemical species	Elementary reactions	NOx Chemistry	Reference
<i>i</i> -cetane	5	1114	4469	No available	Oehlschlaeger et al. 2009
<i>n</i> -hexadecane	5	2115	8157	No available	Westbrook et al. 2009
methyl-cyclohexane	5	1001	4436	No available	Pitz et al. 2007

## 2.1 iso-Cetane detailed kinetics model

In this work, was used the detailed kinetics model from Oehlschlaeger et al. 2009. As described on table 2, the detailed kinetics model for *i*-cetane is composed by 5 chemical elements, allowing 4469 elementary reactions among 1114 chemical species. The model was constructed by using a hierarchical methodology based on previous works from the LNL (Curran et al. 2002; Westbrook et al. 2002; Curran et al. 1998; Westbrook et al. 2009).

This model was validated against experimental data of ignition delay time measurements from a heated high pressure shock tube for  $\phi = 0.5, 1.0, \text{ and } 1.5$  *i*-cetane /air mixtures covering the temperature range of  $879 \text{ K} < T < 1347 \text{ K}$  and pressures from 8 to 47 atm. From figure 7 in Oehlschlaeger's paper, it can be observed that the detailed kinetics model works better for rich mixture conditions, covering both the pressure values and the whole range of temperature.

The detailed kinetics model overpredicts the delay time for stoichiometric composition except around 1000 K. For lean mixture conditions, the best numerical predictions moves to the high temperature range.

## 2.2 Hexadecane detailed kinetics model

The model used in this work for hexadecane ignition delay time simulations cover the pyrolysis and thermal oxidation of *n*-alkanes from C8 to C16. The model, from Westbrook et al. 2009, is also based on previously published works from LNL and based on the chemical kinetics of primary reference fuels (*i*-octane and *n*-heptane) schemes.

The model is composed by 5 chemical elements, allowing 8157 elementary reactions among 2115 chemical species. This large number of elementary reaction is in function of the many kinds of elementary reactions involved in the kinetics model, covering from unimolecular fuel decomposition reactions till reactions of cyclic ethers with OH and HO<sub>2</sub>.

The kinetics model was validated against experimental results from several authors, covering pyrolysis, high and low temperature oxidation in shock tube and rapid compression machine, flow reactor, jet-stirred reactor and pressurized flow reactor. The model reproduces the experimentally observed negative temperature coefficient – NTC behavior for all *n*-alkanes.

## 2.3 Methyl-Cyclohexane detailed kinetics model

The detailed kinetics model for methylcyclohexane used in this work (Pitz et al. 2007) was also based on the model from *i*-octane from Curran et al. 2002. This kinetics model is composed by 5 chemical elements, allowing 4436 elementary reactions among 1001 chemical species.

The model was validated against ignition delay time measured in rapid compression machine at pressures of 10, 15 and 20 atm., temperature range of  $700 \text{ K} < T < 1050 \text{ K}$  at stoichiometric composition. The model considerably overpredicts the ignition delay data. The model does not reproduce the NTC trend observed in the experimental data.

## 3. NUMERICAL RESULTS

The results are based on the numerical performance of the used detailed kinetics models, looking at thermal oxidation parameters like ignition conduct; ignition delay time, cool flame/first ignition stage and negative temperature coefficient behavior.

### 3.1 Main ignition and first stage ignition

Figure 2(a) shows the comparative ignition delay time trends of the three fuel surrogates used in this work at pressure of 20 bar, stoichiometric composition and temperatures between 600 K to 1250 K.

Figure 2(b) the typical two stage ignition behavior observed in all *n*-alkanes from C5 and higher, in this case for hexadecane at 20 bar, stoichiometric composition and initial temperature of 800 K.

Figure 2(a) shows also the first stage ignition of all the fuels simulated in this work. The first stage ignition, as showed in Figure 2(b) is defined in function of the first peak of hydroxyl radical (OH) observed numerically and experimentally.

It can be observed that, for *n*-alkanes (hexadecane in this work) the first stage ignition yield a temperature increase of about 200 K, in the case of *i*-alkanes (*i*-cetane in this work) the first stage ignition yield a temperature increase of about 40 K (Figure 3(b)), very low when compared to the *n*-alkanes temperature increase.

L.R. Cancino, E. Oliveira, M.I. Rocha, A.A.M. Oliveira.

Isocetane, Hexadecane and Methyl-Cyclohexane as Jet-Fuel Surrogates: A Numerical Study of Ignition Delay Time.

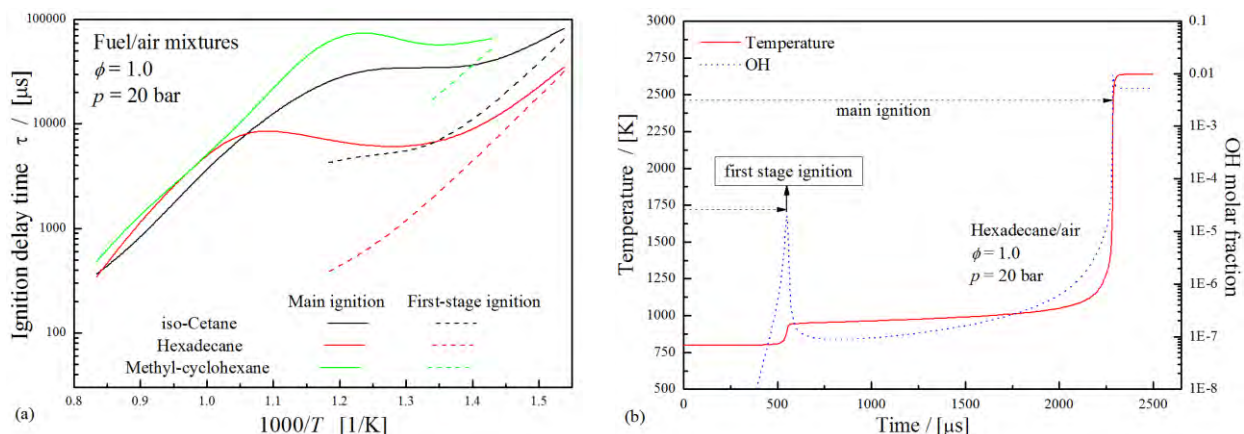


Figure 2. (a) Ignition delay time of the fuels surrogates analyzed in this work at pressure of 20 bar and stoichiometric composition. (b). Ignition delay time (main ignition) and first stage ignition definitions used in this work.

### 3.2 *i*-Cetane – Ignition delay time

Figure 3(a) shows the ignition delay time behavior for *i*-cetane/air mixtures under lean, stoichiometric and rich mixture conditions ( $\phi = 0.6, 1.0$  and  $1.4$ ), at pressures of 5, 10, 20 and 30 bar, covering a temperature range of  $650 \text{ K} < T < 1250 \text{ K}$ .

The first observation is that the ignition delay time of *i*-cetane/air mixtures follows the same trend than other hydrocarbon fuels in terms of pressure dependency (negative pressure dependency)

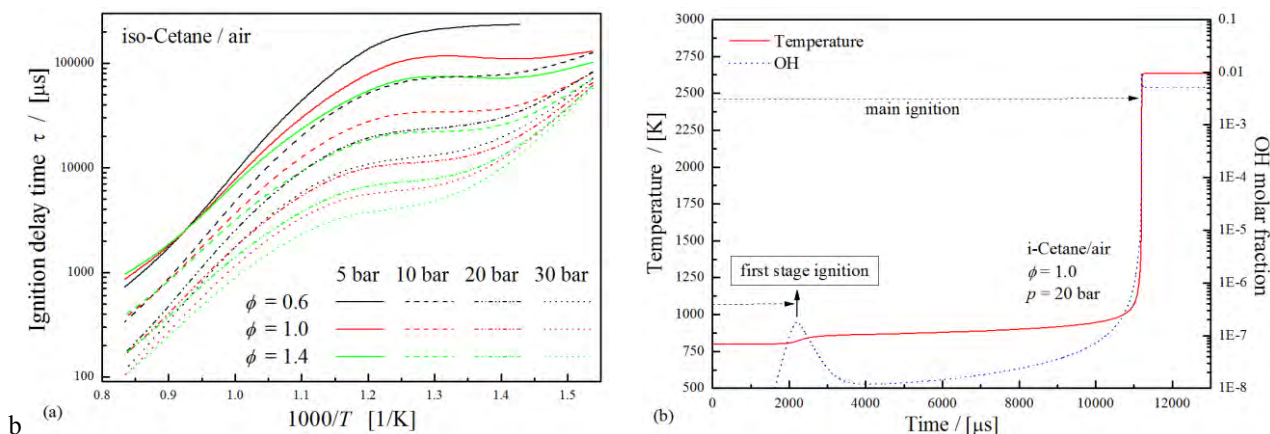


Figure 3. (a) Numerical prediction of IDT for *i*-cetane/air mixtures. (b) Ignition delay time (main ignition) and first stage ignition

It can be observed that there is not observable any negative temperature coefficient behavior, only for high pressures, the model shows some very slight NTC performance.

Also, it can be observed that *i*-cetane shows the same behavior that *i*-octane (branched alkanes). On Figure 3(b) can be observed that the temperature increase associated to the first peak of hydroxyl radical is around 40 K.

### 3.3 Hexadecane – Ignition delay time

Figure 4 shows the numerical results of the thermal oxidation of hexadecane. Figure 4(a) shows the ignition delay time of hexadecane/air mixtures at  $\phi = 0.6, 1.0$  and  $1.4$  (lean, stoichiometric and rich mixture conditions) for pressures of 5, 10, 20 and 30 bar, covering a temperature range of  $600 \text{ K} < T < 1250 \text{ K}$ .

Note that, hexadecane shows the same trend of NTC behavior when compared to lower *n*-alkanes like *n*-heptane. Also, it can be observed that the ignition delay time pressure dependency is negative, as is observed for *n*-heptane.

Figure 4(b) shows the first stage ignition delay time of hexadecane/air mixtures at  $\phi = 0.6, 1.0$  and  $1.4$  (lean, stoichiometric and rich mixture conditions) for pressures of 5, 10, 20 and 30 bar, covering a temperature range of  $600 \text{ K} < T < 1250 \text{ K}$ . It is observed that the first stage ignition follows the trend of the main ignition in terms of pressure dependency.

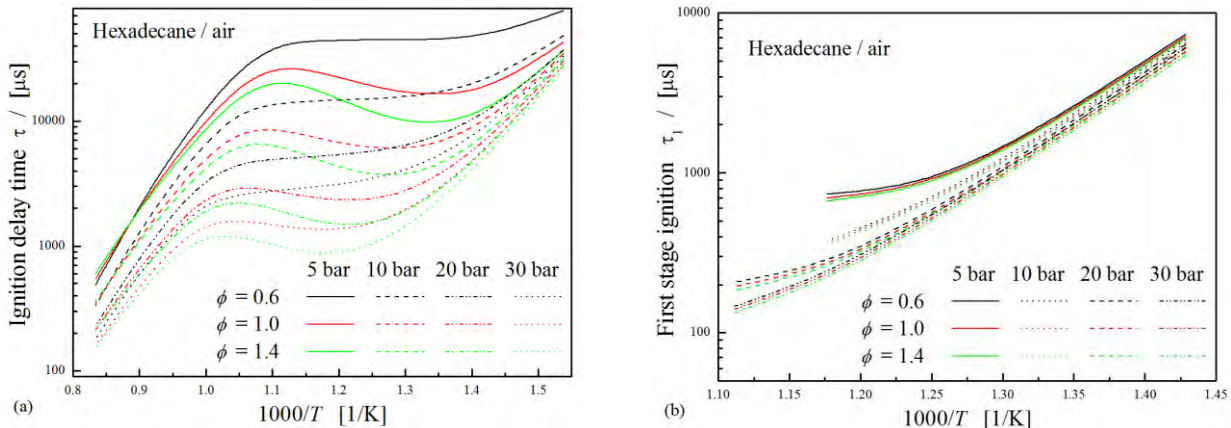


Figure 4. (a) Numerical prediction of IDT for hexadecane/air mixtures (b) First stage ignition for hexadecane/air mixtures

### 3.4 Methyl-Cyclohexane – Ignition delay time

Figure 5 shows the ignition delay time behavior of methylcyclohexane/air mixtures under lean ( $\phi = 0.6$ ), stoichiometric and rich ( $\phi = 1.4$ ) mixture conditions, at pressures of 5, 10, 20 and 30 bar, covering a temperature range between 600 K to 1250 K.

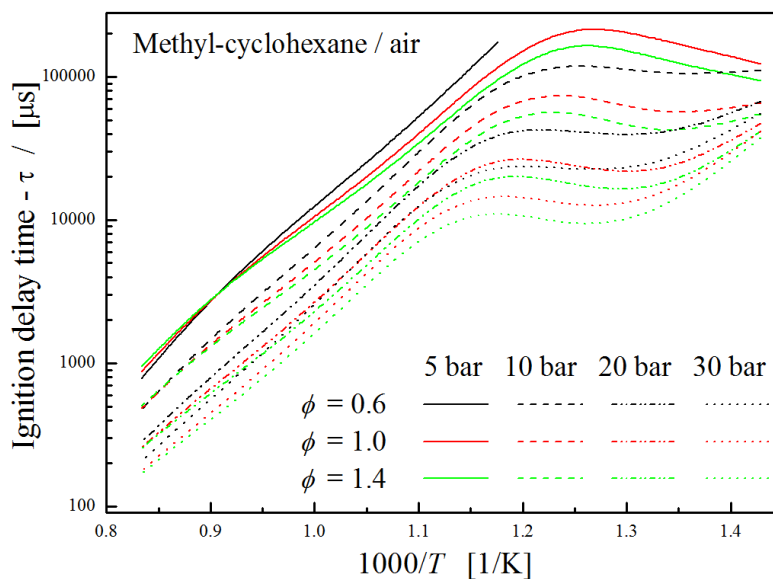


Figure 5. Numerical prediction of IDT for methyl-cyclohexane/air mixtures

In terms of ignition behavior, methyl-cyclohexane shows similar trend to the toluene ignition delay time, with the difference that for toluene, there is not observed any NTC regime.

In Figure 5 it can be observed a slight NTC behavior, and this effect is increased with pressure as occurs with the common hydrocarbons. Also, the methyl-cyclohexane shows very clear negative pressure dependence in terms of ignition delay time.

For lean mixtures and low pressures (5 bar) the detailed kinetics model does not indicate any kinetics event, no ignition is observed.

## 4. DISCUSSION AND CONCLUSION

Several observations can be made in order to discuss and conclude this numerical analysis. The more important aspect is the lack of experimental results in order to perform an extensively validation process of this three chemical species used as fuel surrogates in several works reported in the literature (Colket et al. 2007; Violi et al. 2002).

L.R. Cancino, E. Oliveira, M.I. Rocha, A.A.M. Oliveira.

Isocetane, Hexadecane and Methyl-Cyclohexane as Jet-Fuel Surrogates: A Numerical Study of Ignition Delay Time.

- One of the more important aspects is that the development of detailed kinetics models requires validation from controlled and well established experiments: shock tubes, well stirred reactors, plug flow reactors, constant volume reactors, opposed diffusion flames, etc.
- Especially for methyl-cyclohexane, there is a lack of experimental result in order to improve the detailed kinetics model. The authors of this model (Pitz et al. 2007) observed that the few experimental results obtained in rapid compression machine shows a NTC regime, and the detailed kinetics model is not able to reproduce this trend.
- Another model for *i*-cetane was found in the literature (Ranzi et al. 2005) composed by 6 chemical elements, 14000 elementary reactions among ~500 chemical species. The computational time for analysis of *i*-cetane oxidation by using the Ranzi model is very big, taking approximately 6.5 hours for each temperature, pressure and mixture condition, without including sensitivity analysis in the run (using a 16 GB RAM, intel i7® processor desktop). Of this form, to make the figure 5 in this work will take ~40 days (full time simulation).
- It was observed that the hexadecane (*n*-alkane) follows the well knew NTC regime. This effect is promoted for the increase on the temperature observed in the first peak of radical hydroxyl, activating the low temperature chemistry of linear alkanes and reducing the ignition delay time when the initial temperature is also reduced.
- For the branched alkane, *i*-cetane, it is observed that it follows the numerical and experimental observed trend of *i*-octane (low C8 branched alkane).
- There are necessary sensitivity and reaction path analyses in order to identify the main influencing elementary reaction in order to improve the detailed kinetics model available at literature. A second step of this work is just in this direction.
- Note that, the detailed kinetics models used in this work, were developed for pure fuels, there is necessary a blending process (see Cancino et al. 2009 and 2011) in order to develop detailed kinetics schemes for blends of fuels surrogates.

## 5. ACKNOWLEDGEMENTS

The authors acknowledge the financial support of PETROBRAS.

## 6. REFERENCES

- Cancino, L.R., Fikri, M., Oliveira, A.A.M., Schulz, C., 2009 “Autoignition of gasoline surrogate mixtures at intermediate temperatures and high pressures: Experimental and umerical approaches”. *Proceedings of the Combustion Institute*, Vol. 32, p. 501–508.
- Cancino, L.R., Fikri, M., Oliveira, A.A.M., Schulz, C., 2011 “Ignition delay times of ethanol-containing multi-component gasoline surrogates: Shock-tube experiments and detailed modeling”. *Fuel*, Vol. 90, p. 1238–1244.
- Charles K. Westbrook, C.K., Pitz, W.J., Herbinet, O., Curran, H.J., Silke, E.J., 2009. “A comprehensive detailed chemical kinetic reaction mechanism for combustion of n-alkane hydrocarbons from n-octane to n-hexadecane” *Combustion & Flame* 156 pp.181–199.
- Colket, M., Edwards, T., Williams, S., Cernansky, N., Miller, D.L., Egolfopoulos, F., Linstedt, P., Seshadri, R., Dryer, F.L., Law, C.K., Friend, D.G., Lenhart, D., Pitsch, H., Sarofim, A., Smooke, M., Tsang, W., 2007. “Development of an Experimental Database and Kinetic Models for Surrogate Jet Fuels”. In *45th AIAA Aerospace Sciences Meeting and Exhibit Proceedings*. Reno, NV, USA.
- Curran, H.J., Gaffuri, P., Pitz, W.J., Westbrook, C.K., 1998. “A Comprehensive Modeling Study of n-Heptane Oxidation” *Combustion & Flame* 114 pp.149–177.
- Curran, H.J., Gaffuri, P., Pitz, W.J., Westbrook, C.K., 2002. “A comprehensive modeling study of iso-octane oxidation” *Combust. & Flame* 129 pp.253–280.
- Oehlschlaeger, M.A., Steinberg, J., Westbrook, C.K., Pitz, W.J., 2009 “The autoignition of iso-cetane at high to moderate temperatures and elevated pressures: Shock tube experiments and kinetic modeling” *Combustion & Flame* 156 pp.2165–2172.
- Pitz, W.J., Naik, C.V., Mhaolduin, T.N., Westbrook, C.K., Curran, H.J., Orme, J.P., Simmie, J.M., 2007. “Modeling and experimental investigation of methylcyclohexane ignition in a rapid compression machine” *Proc. Combust. Inst.* 31 pp.267–275.
- Ranzi, E., Frassoldati, A., Granata, S., Faravelli, T., 2005. “Wide-Range Kinetic Modeling Study of the Pyrolysis, Partial Oxidation, and Combustion of Heavy n-Alkanes”, *Ind. Eng. Chem. Res.* 44(14), pp.5170-5183.
- Violi, A., Yan, S., Eddings, E.G., Sarofim, A.F., Granata, S., Faravelli, T., Ranzi, E., 2002. “Experimental formulation and kinetic model for JP-8 surrogate mixtures”. *Combustion Science and Technology*, Vol. 174, Issue 11-12, p. 399-417.
- Westbrook, C.K., Pitz, W.J., Boercker, J.E., Curran, H.J., Griffiths, J.F., Mohamed, C., Ribaucour, M., 2002. “Detailed chemical kinetic reaction mechanisms for autoignition of isomers of heptane under rapid compression” *Proc. Combust. Inst.* 29 pp.1311–1318.

22nd International Congress of Mechanical Engineering (COBEM 2013)  
November 3-7, 2013, Ribeirão Preto, SP, Brazil

Westbrook, C.K., Pitz, W.J., Herbinet, O., Curran, H.J., Silke, E.J., 2009. "A comprehensive detailed chemical kinetic reaction mechanism for combustion of n-alkane hydrocarbons from n-octane to n-hexadecane" *Combustion & Flame* 156 pp.181–199.

## **7. RESPONSIBILITY NOTICE**

The authors are the only responsible for the printed material included in this paper.