



AVIATION AND AUTOMOTIVE FUEL SURROGATES: REVIEW OF NUMERICAL AND EXPERIMENTAL WORKS

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Abstract. *This work presents a review of numerical and experimental works on aviation and automotive fuel surrogates, their chemical kinetics and properties, covering hydrocarbons from C₂ (ethanol) to C₁₆ (iso-cetane). Commercial fuels are usually composed by blends of hundreds to thousands of chemical species, some of them unknown. One strategy to allow for combined numerical and experimental studies consists in proposing a group of chemical species as fuel surrogates, simplifying the complexity of the analysis and allowing simplified numerical and experimental approaches. This review focus on kerosene type Jet-A1 and gasoline. The common chemical species used by the scientific community as surrogates are identified and their chemical characteristics are discussed.*

Keywords: *Fuel surrogates, Chemical kinetics, Fuel research, Combustion.*

1. INTRODUCTION

The engineering and scientific community has been searching for the identification of surrogate fuels that can reasonably represent the performance and emissions behavior of jet fuels (e.g., Jet A, JP-8) in engines (Colket et al. 2007). In summary, there is a current global need of a) alternatives to conventional oil derived fuels, especially those obtained from renewable sources, b) reduction of pollutant and carbon emissions from energy and power systems, and c) additives to reduce engine knock. These improvements can lead a fuel produced from a renewable resource (biomass) that could be sustainably developed in the future, resulting in poor releases of carbon dioxide (CO₂) and very low sulfur content, and appears to have significant economic potential provided that fossil fuel prices increase in the future (Demirbas, 2007).

Part of the effort needed nowadays is centered on understanding the oxidation mechanisms of pure substances, called surrogates, using a combination of simulation and fundamental experiments developed at conditions close to the applications.

Today it is common to find numerical models attempting to represent combustion process of single hydrocarbon fuels, and depending on the desired quality or target of the results, one may find global or detailed kinetics mechanisms. In this direction, many researchers have devoted considerable time studying and proposing global and detailed kinetics models (see, for example, references in Griffiths, 1995 and Simmie, 2003) for pure hydrocarbon oxidation. The number of chemical species that can be present in a real gasoline (for automotive or aviation application) can be, however, in the order of hundreds, involving saturated and unsaturated hydrocarbons including alkanes, cycloalkanes, alkenes, cycloalkenes, aromatic, ethers and esters, components whose identity and amounts are often unknown (Metcalfé et al. 2007).

The well-known kinetic model for pure iso-octane oxidation of Curran et al. (2002) is composed by 857 chemical species allowing 3606 elementary reactions. A detailed kinetics model for a practical fuel involving a hundred of chemical species in the fuel composition would demand a dramatically increase in the number of elementary reactions, making the problem intractable with current computational capabilities. The development of gasoline surrogates is one of the ways to make the development of chemical kinetics mechanisms for practical fuels tractable. A surrogate fuel consists of a mixture of a small number of components that are used to represent the practical fuel and still predict characteristics of the real fuel. These desirable characteristics may include ignition behavior, burning velocity, viscosity, vaporization, and emission such as carbon monoxide, hydrocarbons, soot and nitrogen oxides (Metcalfé et al.

J.G. Oliveira, C.R. Medeiros, L.R. Cancino, E. Oliveira, M.I. Rocha and A.A.M. Oliveira.
Aviation Fuel Surrogates: A Numerical And Experimental Review

2007), as well as thermo-physical and transport properties (color, saybolt, total acid number, % of aromatics, % of sulfur, distillation temperature, flash point, density or gravity, freezing point, viscosity, neat heat of combustion, C/H atom ratio, smoke point, % of naphthalene, cetane index, cooper strip corrosion, thermal stability, existent gum, particulate matter, fuel system icing inhibitor and fuel electrical conductivity among others.

In terms of ignition, the early kinetics modeling studies of n-heptane by Curran et al. (1998) and iso-octane by Curran et al. (2002) covering the parameters used to qualified fuel ignition in automotive applications, the Research Octane Number – RON and the Motor Octane Number – MON, were first attempts to develop gasoline fuel surrogates. The RON and MON scales are both based on primary reference fuels, n-heptane (RON = MON = 0) and iso-octane (RON = MON = 100), and are used to qualify the knocking behavior of real fuels. For diesel engines, a similar classification exists, based on the cetane number.

This classification uses two primary reference fuels: the n-hexadecane (cetane = 100) and the 1-methylnaphthalene (cetane = 0). The 1-methylnaphthalene was later replaced with heptamethylnonane which was calibrated against the original fuels and assigned a cetane number of 15. Of this form, the Cetane Number scale is now defined in terms of volumetric compositions as $CN = \% \text{ n-cetane} + 0.15 * (\% \text{ heptamethylnonane})$. Figure 1 shows the comparison between cetane and octane rating in terms of ignition.

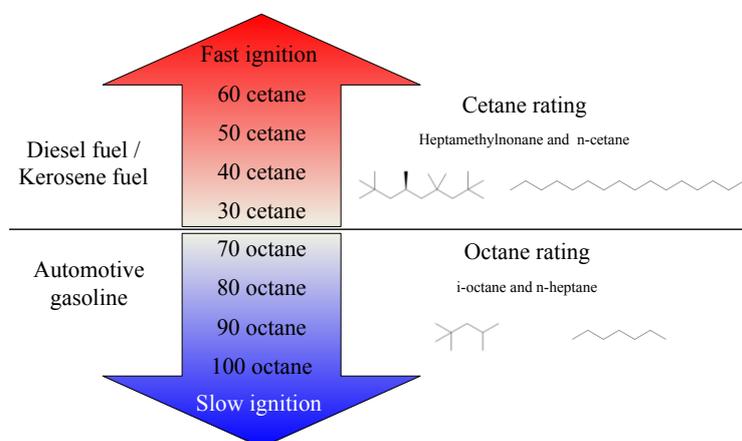


Figure 1. Comparison between cetane and octane rating

It can be observed that C7-C8 is the base-line for octane rating, and C16 is quite the base-line for cetane rating. However, real gasoline/kerosene fuels are not composed only by n-heptane, iso-octane or hexadecane, in fact, real fuels (aviation or automotive) consists of many different classes of saturated and unsaturated hydrocarbons, including straight and branched alkanes (n-paraffins, iso-paraffins), cicloalkanes (naphthenes), alkenes (olefins), cicloalkenes (cycloolefins) and aromatics (Aryl compounds).

In terms of jet fuel surrogates, many proposals exist in the literature, but there has been no consensus of opinion. It has been recognized that if the surrogate (or its) components were identified and agreed upon, then the research community could focus their resources on the development of chemical kinetic models for accurate representation of this surrogate.

In this review, the state of the art in terms of chemical kinetics of fuels surrogates is presented, involving automotive and aviation fuels. However, a big part of this work is devoted to revise the available models for aviation fuel surrogates. This review is presented in two sections, the first one reviewing the single-compound fuel surrogates and the second one reviewing the binary, tertiary and multicomponent blends of compounds as fuel surrogates.

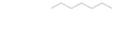
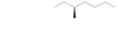
2. SINGLE-COMPOUND FUEL SURROGATES

In order to reduce the chemical complexity, several authors have been working with pure substances. Table 1 summarizes the single-compound fuel surrogates reviewed in this paper. This table shows information about the chemical group, formula, carbons atoms, H to C ratio, molecular weight, CAS number, experimental set-up, stoichiometry, temperature, pressure and dilution conditions used in each investigation. For single and multi ring aromatics, Dagaut et al. 2002(a) studied the toluene oxidation in a jet-stirred reactor at atmospheric pressure.



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Table 1. Single-compound fuel surrogates

Chemical Compound	Formula	Carbon Atoms	H/C Ratio	Molecular Structure	Molecular Weight	CAS number	Exp. Set-up	ϕ	Temperature (K)	Pressure (bar)	Concentration	Reference
Single and multi- Ring Aromatics												
Toluene	C ₇ H ₈	7	1.14		92.14	108-88-3	JSR	0.5 - 1.5	1000 – 1375	1	***	Dagaut et al. 2002
Methyl-Naphthalene	C ₁₁ H ₁₀	11	0.91		142.19	90-12-0	Shock Tube	0.5 - 1.5	1032 – 1445	14 - 62	950 ppm	Wang et al. 2010
Tetralin	C ₁₀ H ₁₂	10	1.20		132.2	119-64-2	JSR	0.5 - 1.5	790 – 1400	1 - 10	1000 ppm	Dagaut et al. 2013
Cyclic Alkanes												
Methyl-CycloHexane	C ₇ H ₁₄	7	2.00		98.19	108-87-2	Shock Tube	0.5 - 2	1200 – 2100	1 - 4	5.25 - 10.50%	Orme et al. 2006
Decalin	C ₁₀ H ₁₈	10	1.80		138.25	91-17-8	Shock Tube	0.5 - 1.0	990 – 1300	9 - 48	***	Oehlschlaeger et al. 2009
Esters												
Methyl Butanoate	C ₅ H ₁₀ O ₂	5	2.00		102.13	623-42-7	Shock Tube	0.25 - 1.5	640 – 949	1 - 4	1.0 - 1.5 %	Dooley et al. 2008
Methyl Octanoate	C ₉ H ₁₈ O ₂	9	2.25		158.24	111-11-5	JSR	0.5 - 2	800 – 1350	1.01	***	Dayma et al. 2011
»	C ₉ H ₁₈ O ₂	9	2.25		158.24	111-11-5	Shock Tube	0.5 - 2.0	1263 – 1672	1 - 10	99% Ar diluent	Rotavera and Petersen, 2013
Methyl Decanoate	C ₁₁ H ₂₂ O ₂	11	2.00		186.29	110-42-9	JSR	0.25 - 2.0	900 – 1800	1 - 10	***	Sarathya et al. 2010
Alkanes												
n-Heptane	C ₇ H ₁₆	7	2.29		100.20	142-82-5	Shock Tube	0.3 - 1.5	550 – 1770	1 - 42	14 - 99% N ₂ diluent	Curran et al. 1998
3 - Methyl- Heptane	C ₈ H ₁₈	8	2.25		114.23	589-81-1	JSR	0.5 - 2	530 – 1220	10	1000 ppm	Karsenty et al. 2010
Iso-octane	C ₈ H ₁₈	8	2.25		114.23	540-84-1	Shock Tube	0.5 - 1	855 – 1269	14 - 59	***	Davidson et al. 2005
n-Undecane	C ₁₁ H ₂₄	11	2.18		156.31	1120-21-4	JRS	0.5 - 2	550 – 1150	10	1000 ppm	Mzé-Ahmed et al. 2012
n-Dodecane	C ₁₂ H ₂₆	12	2.36		170.33	112-40-3	JRS	0.5 - 2	550 – 1150	10	1000 ppm	Mzé-Ahmed et al. 2012
n-cetane (Hexadecane)	C ₁₆ H ₃₄	16	2.13		226.44	544-76-3	Shock Tube	0.5 - 1.5	879 – 1347	8 - 47	700 ppm	Oehlschlaeger et al. 2009
Alcohols												
1 - propanol	C ₃ H ₈ O	3	2.67		60.09	71-23-8	JSR	0.35 - 2	770 – 1190	10	1500 ppm	Galmiche et al. 2011
2-butanol	C ₄ H ₁₀ O	4	2.50		74.12	78-92-2	JSR	0.275 - 4	770 – 1250	10	1000 - 1500 ppm	Togbé et al. 2010
Isobutanol	C ₄ H ₁₀ O	4	2.50		74.12	78-83-1	JSR	0.275 - 4	770 – 1250	10	1000 - 1500 ppm	Togbé et al. 2010
Iso-pentanol	C ₅ H ₁₂ O	5	2.40		88.15	123-51-3	JSR	0.35 - 4	530 – 1220	10	1000 - 1500 ppm	Dayma et al. 2011

New experimental results were obtained over the high temperature range 1000–1375 K, and stoichiometries covering the range of $0.5 < \phi < 1.5$. Using probe sampling followed by on-line and off-line GC analyses, concentration profiles of reactants, stable intermediates and final products were measured. These experiments were then used for the validation process of a detailed kinetic reaction mechanism (120 species and 920 reactions, most of them reversible).

The proposed detailed kinetics model was also used to simulate the ignition of toluene–oxygen–argon mixtures and the burning velocities of toluene–air mixtures, obtaining coherent results. Sensitivity analyses and reaction path analyses, based on species rates of reaction, were used to interpret the results. The routes involved in toluene oxidation were then delineated: toluene oxidation proceeds via the formation of benzyl, by H-atom abstraction, and the formation of benzene, by H-atom displacement yielding methyl and benzene; benzyl oxidation yields benzaldehyde, that further reacts yielding phenyl whereas benzyl thermal decomposition yields acetylene and cyclopentadienyl; further reactions of cyclopentadienyl yield vinylacetylene.

Wanga et al 2010 reported ignition delay time measurements on high pressure shock tube for α -methyl-naphthalene, and α -methyl-naphthalene/n-decane blends at elevated pressures, 14–62 bar, for fuel/air mixtures at different compositions. The shock tube experiments covered IDT measurements for $\phi = 0.5, 1.0, \text{ and } 1.5$ α -methyl-naphthalene/air mixtures (CN = 0) for 1032–1445 K and 8–45 bar and for $\phi = 1.0$ 30%-molar α -methyl-naphthalene/70%-molar n-decane/air mixtures (CN = 58) and 70%-molar α -methyl-naphthalene/30%-molar n-decane/air mixtures (CN = 28) for 848–1349 K and 14–62 bar. Also, a comprehensive kinetic mechanism to describe the oxidation of α -methyl-naphthalene and α -methyl-naphthalene/n-decane blends was developed. Kinetic simulations, based on the comprehensive α -methyl-naphthalene/n-decane mechanism, are in good agreement with measured ignition times. Sensitivity and reaction flux analysis indicate the importance of reactions involving resonance stabilized phenylbenzyl radicals, the formation of which by H-atom abstractions with OH radicals has an important inhibiting effect on ignition. From literature, it can be observed that α -methyl-naphthalene has a lack of kinetic information, however, the development of the detailed kinetics mechanism was useful and the results of the simulation by ignition delay time were quite good, mainly because the complexity of the kinetics scheme and the size of molecules.

Dagaut et al. 2013, reported measurements of stable species concentration at 1 and 10 atm over a range of equivalence ratios ($0.5 < \phi < 1.5$) and temperatures ($790 \text{ K} < T < 1400 \text{ K}$) during the oxidation of tetralin. The oxidation process under these conditions was then simulated using a semidetained kinetics reaction scheme (10.000 elementary reactions and 400 species) deriving from a chemical kinetic model proposed earlier for the oxidation of decalin over a wide range of conditions (jet-stirred reactor, plug-flow reactor, and shock-tube). The Dagaut et al.'s proposed detailed kinetics model shows reasonable agreement with the obtained measurements. Also, the proposed model can also be used to represent tetralin pyrolysis based on a variety of results available in the literature. The study of tetralin in low temperature is necessary, because the conversion fuel is limited. However, the results are in agreement with the jet stirred reactor data. It is important to rise that for the future studies, the proposed model can help mainly if the study involves liquid biofuels containing fractions of naphthenic or naphtheno-aromatics.

For cyclic alkanes, Orme et al. 2006, reported oxidation of methyl-cyclohexane in high-temperature shock tube experiments. Ignition delay times for a series of mixtures, of varying methyl-cyclohexane/oxygen equivalence ratios ($\phi = 0.5, 1.0, 2.0$), were measured over reflected shock temperatures of 1200–2100 K and reflected shock pressures of 1.0, 2.0, and 4.0 atm. A detailed chemical kinetics mechanism was assembled to simulate the shock tube results and flow reactor experiments. Good agreement was observed. Also Orme et al. compared the results with studies of others authors, judge against the increasing and the decreasing of O_2 concentrations, it was in good agreement with the study and in general, with the ignition delay time in a shock tube.

Dooley et al. 2008, studied the autoignition of methyl butanoate in a shock tube at 1 to 4 bar, temperature range of 1250–1760 K at equivalence ratios of 0.25 to 1.5. The fuel concentration was about 1.0 – 1.5%. The study was also extended to rapid compression machine (RCM) experiments over the temperature range of 640–949 K, with pressures from 10 to 40 bar, stoichiometry between $0.33 < \phi < 1.0$ and fuel concentration from 1.59 to 3.13%. The methyl butanoate chemistry was analysed in flow reactor, jet stirred reactor and an opposed-flow diffusion flame to produce experimental data in order to validate the detailed kinetics model. The effects vary according to equivalence ratio, fuel fraction and pressure in a shock tube; in a rapid compression machine, the result is not accurate at all, however, the qualitative aspect is reasonable. Sensitivity and flux analyses pathway overreached the results. Methyl butanoate did not exhibit NTC (Negative Temperature Coefficient) behavior, what is common for long chain methyl esters. Consequently, it is not an ideal fuel surrogate for a detailed study.

Karsenty et al. 2012, studied the oxidation of 3-methylheptane in a jet-stirred reactor. This hydrocarbon with others isomers are candidate to be diesel. The temperature used in the study was the range of $530 \text{ K} < T < 1220 \text{ K}$ at pressures about 10 bar and equivalence ratio of $0.5 < \phi < 2$. Under similar conditions, 3-methylheptane oxidizes slower than 2-methylheptane. This study allowed to understand the effect of methyl substitution in forming species: occurring peroxidation, forming cyclic ether called 2,5-dimethyl-2-ethyl-tetrahydrofuran under cool-flame conditions of path analyses

Togbé et al. 2010, studied the oxidation of methyl octanoate-1-butanol at 10 bar of pressure, equivalence ratio of $0.5 < \phi < 2$ and temperatures between of $560 \text{ K} < T < 1190 \text{ K}$ by using a jet-stirred reactor as a experimental setup.

J.G. Oliveira, C.R. Medeiros, L.R. Cancino, E. Oliveira, M.I. Rocha and A.A.M. Oliveira.
Aviation Fuel Surrogates: A Numerical And Experimental Review

Flame ionization detection (FID) analyses with thermal conductivity (TCD), mass spectrometry (MS), off-line gas chromatography (GC) and Fourier transform infrared spectrometry (FTIR) were used to determinate the concentration profiles of reactants, intermediates and final products in function of temperature and low-pressure. A detailed kinetics models allowing 4545 reactions among 1098 species was proposed.

Sarathy et al. 2011 report new combustion data for methyl decanoate in an opposed-flow diffusion flame. An improved detailed chemical kinetic model for methyl decanoate combustion was developed, which serves as the basis for deriving a skeletal mechanism via the direct relation graph method (DRG). The novel skeletal mechanism consists of 648 species and 2998 reactions. The skeletal mechanism reproduces the behavior of the fully detailed mechanism in plug flow and stirred reactors for temperatures of $900 \text{ K} < T < 1800 \text{ K}$, equivalence ratios of $0.25 < \phi < 2.0$, and pressures of 1 and 10 bar. This mechanism well predicts the methyl decanoate opposed-flow diffusion flame data. The results from the flame simulations indicate that methyl decanoate is consumed via abstraction of hydrogen atoms to produce fuel radicals, which lead to the production of alkenes. The ester moiety in methyl decanoate leads to the formation of low molecular weight oxygenated compounds such as carbon monoxide, formaldehyde, and ketene. Of particular interest was the production of C5–C8 1-alkenes which are formed after β -scission of fuel radicals. The production of low molecular weight oxygenated compounds such as formaldehyde, ketene, and isomers of C₂H₄O was also observed.

Oehlschlaeger et al. 2009 Reported high pressure shock tube ignition delay time measurements for decalin/air mixtures at elevated-pressure conditions, relevant to practical combustion engines, for varying pressure (9-15 and 35-48 bar), equivalence ratio of $0.5 < \phi < 1.0$, and temperature ($990 < T < 1300 \text{ K}$). An automatic kinetic generator, the MAMA code, was used to develop a semi-detailed submechanism for decalin decomposition at high-temperature conditions. The kinetics simulations were then compared to the measured ignition times observing adequate agreement. Sensitivity analysis indicates limited importance of decalin unimolecular decomposition and hydrogen abstraction from decalin and moderate importance of the decomposition of C₁₀H₁₇ radicals in predicting ignition times.

Mzé-Ahmed et al. 2012 reported JSR experimental data of two large n-alkanes. In this study, the kinetics of oxidation of n-undecane and n-dodecane at pressure of 10 bar, temperatures ranging from $550 < T < 1150 \text{ K}$, at a constant residence time (τ) of 1 s, and for three equivalence ratios ($\phi = 0.5, 1.0, \text{ and } 2.0$) was studied. Chemical analyses by Fourier transform infrared (FTIR) spectrometry and gas chromatography allowed for the measurement of the mole fraction of reactants, stable intermediates and final products as a function of the temperature. They observed similar behavior for the oxidation of n-undecane, n-dodecane, and Jet A-1 in a JSR. It was shown that the pure n-alkanes oxidized faster than Jet A-1 under cool-flame conditions and intermediately yielded more ethylene.

Oehlschlaeger et al. 2009 report new experiments and kinetic modeling results for the autoignition of iso-cetane at elevated temperatures and pressures relevant to combustion in internal combustion engines. Ignition delay time measurements were made in reflected shock experiments in a heated shock tube for $\phi = 0.5, 1.0, \text{ and } 1.5$ iso-cetane/air mixtures at temperatures ranging from 879 to 1347 K and pressures from 8 to 47 atm. A new kinetic mechanism for the description of the oxidation of iso-cetane is presented that is developed based on a previous mechanism for iso-octane. The agreement between mechanism predictions and measured ignition delay times is very good, particularly in light of the large size and complexity of the mechanism and because there has been no adjustment to rate parameters for improved agreement with experiment. The agreement for such a large alkane suggests that the rate coefficient rules developed for aliphatics can be extended to other compounds with confidence at high to moderate temperatures. The data and mechanism contribute toward the kinetic understanding of large alkane compounds found in transportation fuels and will be useful for developing surrogate mixtures for diesel, jet fuels, and other fuels containing large alkanes. Additionally the presented reaction mechanism completes a set of reaction mechanisms for cetane and octane rating reference fuels. While there is agreement demonstrated here between experiment and kinetic simulation for the case of the high- to moderate-temperature ignition of iso-cetane, there is still significant opportunity for additional experimental and kinetic modeling work related to large branched alkanes.

Davidson et al. 2005, studied the ignition delay times measured in a Shock tube for iso-octane/air and toluene/air at conditions similar to those found in homogeneous charge compression ignition (HCCI) engines. The measurements were obtained over the temperature 855–1269 K, pressure 14–59 atm, and equivalence ratios of 0.5 and 1 in synthetic air. The iso-octane ignition delay times are in excellent agreement with existing measurements and modeling by literature (no comparable high-pressure data exist for toluene/air). Modeling by Pitz et al. 2001 and Dagaut et al. 2002 (b) significantly over-predicts the toluene/air ignition delay times at $\phi = 1$. The large pressure range of the current measurements permits determination of the pressure dependence of ignition delay time at the temperatures and pressures of direct interest in HCCI engine simulations. Detailed examination of the pressure–time profiles shows evidence of significant pre-ignition energy release in both the iso-octane/air and toluene/air systems. The correlated iso-octane/air data were found to scale with pressure as $p^{-0.77}$ for both $\phi = 1.0$ and 0.5. The correlated toluene/air data were found to scale with pressure as $p^{-0.93}$ for $\phi = 1.0$, but as $p^{-0.5}$ for $\phi = 0.5$. The activation energy for both iso-octane/air and toluene/air varies strongly with ϕ , and this indicates that the dominant chemistry in the $\phi = 1.0$ systems is different than that occurring in the lean $\phi = 0.5$ case. Evidence of significant negative temperature coefficient (NTC) behavior was observed in the high-pressure (~50 atm) iso-octane/air data.

For methyl octanoate, a model compound for biodiesel fuels, Dayma et al., 2011 reported new experimental results, consisting of concentration profiles of stable species as a function of temperature, obtained for the oxidation process in a jet-stirred reactor (JSR) at 0.101 MPa, $0.5 < \phi < 2$ and temperature ranging from 800 to 1350 K. In addition, new experimental data, consisting of concentration profiles of stable species as a function of distance from fuel port, generated in an opposed-flow diffusion flame at 0.101 MPa are presented. A detailed chemical kinetic model was developed with 383 chemical species and 2781 chemical reactions. Experimentally, the oxidation of methyl octanoate in the JSR at atmospheric pressure does not show low temperature and NTC behavior, whereas hot ignition occurs at about 800 K. The modeling results are in reasonably good agreement with the experimental data, describing the intermediate species measured in the jet-stirred reactor and in opposed-flow diffusion flame experiments. More recently, Rotavera and Petersen, 2013 studied the ignition behavior and excited-state species profiles of pure and blended methyl octanoate, n-nonane, and methylcyclohexane (MCH) and extended to include two ternary blends of the fuels using 5% and 20% (vol.) under stoichiometric conditions. A heated Shock tube was used over a range of temperature and equivalence ratio ($\phi = 0.5, 1.0, 2.0$) at pressures near 1 and 10 atm. Under near-atmospheric pressure, ignition delay times were of the following order for the pure fuels: methyl octanoate < n-nonane < methylcyclohexane. Experimental results indicate that the ignition behavior of the higher-order methyl ester approaches that of the higher order linear alkane with increased pressure regardless of equivalence ratio. Methyl octanoate also displayed significantly lower pressure dependence relative to the linear alkane and the cycloalkane species. Both of these results are supported by model calculations. Measurements indicated that blending of methyl octanoate with n-nonane and methylcyclohexane impact ignition results more strongly under near-atmospheric pressure, and causes a smaller effect at 10 atm, above 1400 K. The study provides the first shock-tube data for a ternary blend of a linear alkane, a cycloalkane, and a methyl ester. A recent study by Galmiche *et al.* 2011 reported an experimental and detailed kinetic modeling study of the oxidation of 1-propanol. In a pressurized jet-stirred reactor (JSR) the concentration profiles of stable species (reactants, intermediates, and final products) at 10 atm, temperatures ranging from 770 K < T < 1190 K and equivalence ratios ($\phi = 0.35$ -2) was measured. A combustion bomb was used to measure burning velocities of 1-propanol/air mixtures at pressures of $p = 1$ -10 bar and temperature at 423 K (temperature of $T_i = 423$ K, which is higher than the boiling temperature of 1-propanol = 370 K), over a range of equivalence ratios ($0.7 < \phi < 1.4$) and at 1 bar for temperatures from 323 K < T < 473 K. The JSR experiments were modeled using the Chemkin II PSR code and the burning velocities were modeled using the Premix laminar flame code. Their mechanism involved 1116 reversible reactions and 141 species, where in the 1-propanol oxidation it initially reacts via thermal decomposition involving C-O and C-C bond breaking and concerted water elimination. Initiation with molecular oxygen and propagation reactions via H-atom abstraction with simple species X (H, O, OH, HO₂, CH₃, HCO, CH₂OH, CH₃O, and C₂H₅), was included, yielding hydroxypropyl and propoxy radicals ($X + C_3H_7OH \leftrightarrow HX + C_3H_7O$ and C_3H_6OH), also a thermal decomposition of these radicals and oxidation by molecular oxygen were included in the kinetic scheme. Laminar burning velocities were measured for stoichiometric 1-propanol/air mixtures and it varied as $p^{-0.23}$, that is consistent with the literature data available for C1-C6 alcohols. The effect of temperature and total pressure on the burning velocity of nearly stoichiometric flames ($\phi = 1.05$) indicated that increasing the initial temperature increases the burning velocity, the burning velocity is increased by a factor of 2 by changing the initial temperature from 323 K to 473 K. The kinetic mechanism yielded modeling results in reasonably good agreement with experimental data obtained in a JSR and a combustion bomb, although some intermediates were not well-predicted.

In another work, Togbé *et al.* 2010 (a), reported the experimental kinetics of oxidation of two butanol isomers (2-butanol and isobutanol) using a fused silica jet stirred reactor (JSR). The experiments were performed in the temperature range of 770 K < T < 1250 K, at 10 atm, for equivalence ratios in the range of $0.275 < \phi < 4$, and with an initial fuel concentration of 1000 or 1500 ppm. The experiments showed similar rates of consumption for 1-butanol, 2-butanol, and isobutanol, whereas significant variations were observed for product formation and relative concentration. Isobutanol produce more formaldehyde than 2-butanol. Many routes can yield formaldehyde: oxidation of methyl radicals to form CH₃O and CH₂OH that in turn yield CH₂O. Acetaldehyde was mainly formed from the oxidation of 2-butanol, that could occur via decomposition of C₄H₉O and C₄H₈OH radicals to form acetaldehyde and ethyl. The 2-Methyl-propanal was the second most important aldehyde produced in the experiments, but it is only formed from isobutanol. Kinetic modeling was performed using a reaction mechanism taken from the literature. A reasonable agreement between the present experimental results and the computation was observed for isobutanol, whereas the rate of oxidation of 2-butanol was significantly over predicted by the kinetic model.

Dayma et al. 2011 studied experimental and detailed kinetic modeling of isoamyl alcohol (isopentanol or 3-methylbutan-1-ol) oxidation in a Jet-Stirred Reactor at elevated pressure. Concentration profiles of stable species were measured in a JSR at 10 atm over a range of equivalence ratios ($0.35 < \phi < 4$) and temperatures (530 K < T < 1220 K). The experiments showed no cool flame oxidation under the present conditions. The oxidation of isopentanol produces much less acetaldehyde than ethanol, whereas formaldehyde was produced in quantities similar to those reported earlier for the oxidation of C3-C6 alcohols under similar conditions. The oxidation process was modeled using an extended detailed chemical kinetic reaction mechanism (2170 reactions involving 419 species) derived from a previously proposed scheme for the oxidation of a variety of fuels. The proposed mechanism shows good agreement with the

J.G. Oliveira, C.R. Medeiros, L.R. Cancino, E. Oliveira, M.I. Rocha and A.A.M. Oliveira.
Aviation Fuel Surrogates: A Numerical And Experimental Review

present experimental data. To fully assess the validity of the proposed scheme, ignition data and burning velocities are needed for isoamyl alcohol.

Togbé et al. 2010 (b) studied the kinetics of oxidation of a biodiesel-biobutanol surrogate fuel (methyl octanoate/1-butanol) experimentally in a jet-stirred reactor (JSR) at 10 atm, at a constant mean residence time of 0.7 s, over the temperature range 560-1190K, and for several equivalence ratios ranging from 0.5 to 2. The oxidation of this fuel in these conditions was modeled using a detailed chemical kinetic reaction mechanism consisting of 4545 reactions and 1098 species. The proposed kinetic reaction mechanism generally yielded a good representation of the kinetics of oxidation of this biodiesel-biobutanol surrogate under the present conditions. The kinetic modeling was used to delineate the reactions enhancing the low-temperature oxidation of 1-butanol, important for diesel and Homogeneous Charge Combustion Ignition (HCCI) engine applications. The present results also indicated that the methyl octanoate-1-butanol mixtures are less prone to emitting acetaldehyde than the corresponding methyl octanoate-ethanol mixtures oxidized in a JSR and a very similar formaldehyde maximum concentrations (152 and 167 ppm, respectively, for the MO-ethanol and MO-1-butanol mixtures). This result is of interest in terms of air quality preservation since acetaldehyde can contribute to tropospheric ozone formation.

Dagaut and Togbé 2008 investigated the kinetics of oxidation of ethanol-gasoline surrogate mixtures (85-15 vol %) by using a fused silica jet-stirred reactor. One representative of each class constituting E85 gasoline was selected. These constituents were iso-octane, toluene, 1-hexene, and ethanol. The experiments were performed in the temperature range of 770 K < T < 1220 K, at 10 bar, at four equivalence ratios ($\phi = 0.3, 0.6, 1, \text{ and } 2$), and with an initial fuel concentration of 0.2 mol %. This work shows that the high-temperature oxidation of this E85 surrogate is similar to that of ethanol, as a result of the high initial concentration of ethanol in the fuel. Acetaldehyde was found to be an important intermediate formed during the oxidation of this E85 surrogate fuel, as a result of the oxidation of ethanol, the main component in this E85 surrogate fuel; its intermediate concentration is much higher than that yielded from the oxidation of the ethanol-free gasoline surrogate, in line with SI engine data.

3. BINARY AND MULTICOMPONENT BLENDS OF FUEL SURROGATES

In terms of binary, tertiary and multicomponent blends of fuels surrogates, it can be found a lot of numerical and experimental approaches by using many kind experimental set-ups. Every research group has been formulated different mixtures of pure fuels attempting to reach “good agreement” between experimental results obtained with real fuels and surrogate fuels. At the literature, it can be found simple binary mixtures (Aachen surrogates) or very complex mixtures allowing twelve pure substances (Wood et al. 1989), some of them trying to match the physical/chemical composition in function of the quantities of paraffins, mono and cycloparaffins, benzenes, naphthas, etc. Table 2 from Colket et al. 2007 shows the average composition of real Jet A fuel taking into account 55 samples around the world. The second column on table 2 shows the average “Jet-A” made by mixing equal volumes of Jet-A from 5 different manufactures. Table 3 shows a summarized spectrum of 17 fuel surrogates formulated for different purposed, aviation or automotive application.

Table 2. Composition results for 55 word survey fuels (Adapted from Colket et al. 2007)

	World survey average, vol%	Composite Jet A blend
Parafins ($n - + i -$)	58.78	55.20
Monocycloparaffins	10.89	17.20
Dicycloparaffins	9.25	7.80
Tricycloparaffins	1.08	0.60
alkyl benzenes	13.36	12.70
indans + tetralins	4.90	4.90
Naphthalene	0.13	< 0.20
Substituted naphthalenes	1.55	1.30

Wood et al. (1989) formulate a 14 pure components jet surrogate based on the distillation curve and compound class composition of a petroleum derived JP4 jet fuel. The goal was to establish a fuel of controlled composition for the modeling of JP4 combustion leaving into account physical and chemical properties.

Violi et al. 2002 developed a surrogate mixture to represent JP-8. A surrogate blend of six pure hydrocarbons was found to adequately simulate the distillation and compositional characteristics of a practical JP-8.



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Table 3. Multicomponent aviation and automotive fuel surrogates

		Wood et al. (1989) Vol%	Violi et al. (2002) Utah Surrogates Vol%		Colket et al. (2007) Vol%		Aachen Surrates mass%	Agosta et al. (2004) Vol%	Cancino et al. (2009) Vol%	Fikri et al. (2008) Vol%	Vanhove et al. (2006) mol%			Cancino et al. (2011) Vol%	
ethanol	C ₂ H ₅ OH								40	20				25	10
n-heptane	C ₇ H ₁₆								10.2	18					22
n-decane	C ₁₀ H ₂₂	2.5	0	25	50	34	80								
n-undecane	C ₁₁ H ₂₄														
n-dodecane	C ₁₂ H ₂₆	25	30	25	60		80	43							
n-tridecane	C ₁₃ H ₂₈	10													
n-tetradecane	C ₁₄ H ₃₀	5	20	20											
n-pentadecane	C ₁₅ H ₃₂	5													
iso-octane	C ₈ H ₁₈		10	5				27	37.8	62	65	82	47	75	30
iso-cetane	C ₁₆ H ₃₄														
1-hexene	C ₆ H ₁₂										18	30	18		
di-iso-butylene	C ₈ H ₁₆														13
butyl cyclohexane	C ₁₀ H ₂₀				25	33									
methyl-cyclohexane	C ₇ H ₁₄		20	5	20			15							
n-propyl cyclohexane	C ₉ H ₁₈														
n-heptyl cyclohexane	C ₁₃ H ₂₆	11													
n-pentyl cyclohexane	C ₁₁ H ₂₂	11													
decalin	C ₁₀ H ₁₈	11.5													
toluene	C ₇ H ₈			20							35	70	35		25
m-xylene	C ₈ H ₁₀		15												
o-xylene	C ₈ H ₁₀				20										
1,3 diisopropyl benzene	C ₁₂ H ₁₈	3													
1,2,4-trimethylbenzene	C ₉ H ₁₂						20	20							
n-propyl benzene	C ₉ H ₁₂														
n-butyl benzene	C ₁₀ H ₁₄				25	33									
1-phenyl hexane	C ₁₂ H ₁₈	5													
tetralin	C ₁₀ H ₁₂	9.5	5												
1-methyl naphthalene	C ₁₁ H ₁₀	1.5						15							

A hierarchically constructed kinetic model already available for the oxidation of alkanes and simple aromatic molecules (benzene, toluene, ethylbenzene, xylene, etc.) was extended to include methylcyclohexane and tetralin as new reference fuel components. The kinetic model was then validated through comparisons with experimental data for the pure components and it was also used to verify and predict the structures of laminar premixed flames of different pure components as well as conventional kerosene fuels. The jet surrogates formulations are also known as Utah surrogates and have been experimentally and numerically tested by several research groups.

Colket et al. 2007 formulated three ternary mixtures of jet fuels composed by (a) n-dodecane / methylcyclohexane / o-xylene at 60%/20%/20%, (b) n-decane / buthylcyclohexane / butylbenzene at 50%/25%/25% and (c) n-decane / buthylcyclohexane / butylbenzene at 34%/33%/33% (Vol%). Those surrogates were then tested against reactivity data of real jet fuels. The interesting thing in the work of Colket et al. is the introduction to a palette of compounds from which a surrogate fuel might be constructed.

Agosta et al. 2004 investigated the autoignition and combustion behaviour of full boiling range hydrocarbon fuels. The work was focused on the selection of possible components of a surrogate that reproduces the reaction behavior of typical real fuels. n-dodecane and iso-cetane were the reference components for the different alkane classes, while methylcyclohexane and decalin represented naphthenes and alphas-methylnaphthalene represented aromatics. Several oxidation results were obtained in a pressurized flow reactor both for neat components and selected mixtures. The reactivity maps of the different experiments were reported in terms of CO production. The experimental results clearly confirm that autoignition properties of the mixture cannot be simply reproduced by linear blending rules. The different mixtures used by Agosta et al. 2004 are known as Drexel Surrogates and have been used and tested against experimental works from other fuel research groups.

Cancino et al. 2009 reported experimental and numerical results of ignition delay time of a ternary mixture composed by ethanol / n-heptane / iso-octane at 40%/10.2%/37.8% Vol%, with a calculated octane number of 98.8. The experiments were carried out in stoichiometric mixtures in air behind reflected shock waves in a heated high-pressure shock tube. Initial reflected shock conditions were as follows: temperatures of 690–1200 K, and pressures of 10, 30 and 50 bar, respectively. The low percentage of n-paraffins did not induce the ignition behavior at low temperatures to negative temperature coefficient regime.

Fikri et al. 2008 reported ignition times measured in high-pressure shock-tube experiments for fuel blends of n-heptane (18%) / isooctane (62%) / ethanol (20%) by liquid volume (14.5%/44.5%/41% by mole fraction) and n-heptane (20%) / toluene (45%) / isooctane (25%) / diisobutylene (10%) by liquid volume (17.5%/55%/19.5%/8.0% by mole fraction). These fuels have octane numbers comparable to a standard European gasoline of 95 RON and 85 MON. The experimental conditions cover temperatures from 690 to 1200 K and pressures at 10, 30, and 50 bar. The obtained ignition time data were then scaled with respect to pressure and compared to previous results reported in the literature.

Vanhove et al. 2006 investigated the oxidation and autoignition of five undiluted stoichiometric mixtures, n-heptane/toluene, isooctane/toluene, isooctane/1-hexene, 1-hexene/toluene, and isooctane/1-hexene/toluene, in a rapid compression machine below 900 K. Ignition delay times of two- and one-stage autoignition were then measured and compared to those for pure hydrocarbons. It was observed that the largest influence of mixing was in the region of the negative temperature coefficient. Intermediate products also were analyzed. The main reaction paths of low-temperature co-oxidation were then discussed according to current knowledge of the oxidation paths of pure hydrocarbons. It was found that the influence of toluene on the temperature coefficient of the first stage of ignition of isooctane cannot be accounted for by the current theories of low-temperature autoignition. Each hydrocarbon generates a pool of radicals whose reactivity and selectivity toward further attack changes with temperature and with the family of hydrocarbons. The overall behavior of mixtures may result from changing competition for HO₂ and OH as temperature increases during the delay time.

Cancino et al 2011 reported ignition delay times for binary (ethanol / iso-octane, 25%/75% by liquid volume) and quinary (iso-octane/ toluene/n-heptane / diisobutylene / ethanol, 30%/25%/22%/13%/10%) gasoline surrogate fuels in air, under stoichiometric conditions behind reflected shock waves. The investigated post-shock temperature ranges from 720 to 1220 K at pressures of 10 bar for the binary mixture and 10 bar and 30 bar for the quinary mixture. Multiple regression analysis of the data indicates global activation energy of ~124 kJ/mol for the binary mixture and ~101 kJ/mol for the quinary mixture and a pressure dependence exponent of -1.0 was obtained for the quinary mixture. The measurements were compared to predictions using a proposed detailed kinetics model for multicomponent mixtures that is based on the reference fuels (PRF) model as a kernel and incorporates sub-mechanisms to account for the chemistry of ethanol, toluene and diisobutylene. The model was tested using the measured ignition delay times for the surrogate fuels. Additional comparisons are based on literature data for other fuel combinations of the single constituents forming the quinary surrogate to insure that the modified mechanism still correctly predicts the behavior of simple fuels. The proposed model reproduces the trend of the experimental data for all pure fuels and blends investigated in this work, including the pressure dependence.

4. CONCLUDING REMARKS

There are many conclusions and considerations that can be made after this compilation of information, in terms of simulation and experimental data.

- 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.
- In terms of ignition delay times, it was observed that negative temperature coefficient is present from small/medium n-alkanes and also in the large n-alkanes (C7 to C16). For branched alkanes, also the trend of experiments is similar from small/medium i-alkanes and also in the large i-alkanes. (C8 to C16).
- The low temperature oxidation regime is very important in the formulation of a fuel surrogate. There are large temperature gradients in combustion devices during operation, and the fuel can spend considerable time in one or both of the low and intermediate temperature regimes and of this form, the oxidation chemistry in the lower temperature regimes can have a significant role in the overall combustion process, in some cases accounting for substantial heat release and grossly changing the input conditions to the high temperature zone.
- Aromatic hydrocarbons are also major constituents of distillate fuels (i.e. typically aromatics comprise 20% of JP-8). The selected aromatic hydrocarbon is the bicyclic compound α -methyl-naphthalene, the former low end reference compound of the cetane scale.
- From table 3, it can be observed that n-decane (C₁₀H₂₂) have been reported 5 times as jet fuel surrogate, n-docecane (C₁₂H₂₆) 6 times, iso-octane (C₈H₁₈) 11 times, methylcyclohexane (C₇H₁₄) 4 times, toluene (C₇H₈) 5 times. Those are the chemical species more used by the scientific community for composition of fuel surrogates.
- Many research groups have been done comparison between real aviation/automotive fuel vrs single-component (pure fuel) surrogates, some of them obtaining good results.
- A large data set of experimental and detailed kinetic modeling data is available for the formulations of fuel surrogates. However, more data are still necessary in biofuel surrogates as well as in binary and multicomponent blends.
- Measurements for the kinetics of oxidation of aviation biofuel surrogates would be useful. Further improvements of the existing biofuel surrogates are still necessary although the progress that was made in the recent years.
- On this way, biofuel engine requires an improvement to understand the combustion properties and the combustion pathway, to find bioderived liquid fuels constituents that reproduce physical and chemical proprieties of the current fossil fuels (high energy density, low hydroscopic and good mixes with hydrocarbons).
- Isoamyl alcohol (isopentanol or 3-methylbutan-1-ol) that can be biologically produced is among the possible alcohols usable as an alternative fuel in internal combustion engines. It has a higher energy density than smaller alcohols (ca. 28.5 MJ/L, as compared to ca. 21 MJ/L for ethanol and 27 MJ/L for 1-butanol). It is less hydroscopic than ethanol and mixes better with hydrocarbons.
- 1-propanol, which is a renewable alcohol usable as an alternative to petrol-derived gasoline.
- For instance, much of the previous work has focused on the highly branched iso-octane (three substituted methyl groups) and here the highly branched iso-cetane (seven substituted methyl groups). However, many branched alkanes found in commercial fuels, particularly Fischer–Tropsch fuels, contain alkanes with only one or two methyl substitutions. Hence, experimental and modeling studies should be extended to less highly branched large alkanes. Additionally, ignition time data is needed at lower temperatures and speciation data is needed at all conditions (low to high temperature and atmospheric to high pressure).
- Iso-cetane (2,2,4,4,6,8,8-heptamethylnonane, C₁₆H₃₄) is a highly branched alkane reference compound for determining cetane ratings. It is also a candidate branched alkane representative in surrogate mixtures for diesel and jet fuels.
- Decalin is a model compound for bicyclic naphthenes found in jet fuels and coal-, oil-shale-, tar-sand derived fuels, and it is also a potential endothermic fuel for hypersonic flight. Additionally, decalin is a reference component in surrogate mixtures of jet fuels.
- For alkanes mixtures surrogates was observed that the largest influence of mixing was in the region of the negative temperature coefficient when compared to single components.
- The low percentage of n-paraffins did not induce the ignition behavior at low temperatures to negative temperature coefficient regime in gasoline surrogates.
- Once most of the studies report results for gasoline surrogates, the improvement in combustion of large hydrocarbons is becoming necessary on studies of jet fuel surrogates.

- The LabCET group now is focusing its efforts on studying new constituents (from biomass) to assemble at fuel surrogates. Aiming to reach biofuels that can lead the decreasing of fuel consumption and increasing the potency, through studies of kinetic oxidation and mole fraction profiles, delay times, flame speeds, and others.

5. ACKNOWLEDGEMENTS

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J.G. Oliveira, C.R. Medeiros, L.R. Cancino, E. Oliveira, M.I. Rocha and A.A.M. Oliveira.
Aviation Fuel Surrogates: A Numerical And Experimental Review

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