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OXIDATION KINETICS OF MIXTURES OF ISO-OCTANE WITH ETHANOL OR BUTANOL IN A JET-STIRRED REACTOR: EXPERIMENTAL AND MODELING STUDY.

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Abstract

The kinetics of oxidation of mixtures of *iso*-octane with ethanol or 1-butanol (25/75, 50/50, and 75/25 % in vol.) were studied experimentally using a fused silica jet stirred reactor. The experiments were performed in the temperature range 770-1190 K, at 10 atm, at an equivalence ratio of 1. A kinetic modeling was performed using a reaction mechanism resulting from the merging of validated kinetic schemes for the oxidation of the components of the present mixtures (*iso*-octane, ethanol, and 1-butanol). Good agreement between the experimental results and the computations was observed under the present conditions. Reaction path analyses and sensitivity analyses were used to interpret the results.

Introduction

The increase of pollutants and carbon dioxide emissions from ground transportation engines operating with fossil fuels is a major concern (Barker 2007; Fontaras and Samaras 2007; Gorham 2002; Iliuc 2008; Singh et al. 2008). Over the last two decades the inclusion of non-fossil fuel compounds was increasingly used to reduce carbon (Low and Isserman 2009) and mixtures of a variety of oxygenates with petrol gasoline is frequently used. Among these oxygenates, ethanol is the most important gasoline component. However, its increasing use as a fuel raised concerns since relatively large amounts of ethanol and acetaldehyde may be present in engine exhausts (Farrell et al. 2006; Jacobson 2007; Kim and Dale 2006; Magnusson et al. 2002; Niven 2005; von Blottnitz and Curran 2007; Winebrake et al. 2001). More recently, 1-butanol was proposed for blending with gasoline, because of its high energy content (27 MJ/L compared to ≈21 MJ/L for ethanol) and its low vapor pressure (Reid values of 0.33 psi for 1-butanol compared to 2 psi for ethanol, and 4.5 psi for gasoline; 1 psi = 0.06894 bar) (BP and Dupont 2006). Moreover, the interest for producing butanol by advanced fermentation techniques is increasing (Ezeji et al. 2007; Qureshi and Maddox 1995; Tashiro et al. 2005; Tashiro et al. 2007). For engine combustion experiments and modeling simple surrogates are frequently preferred. In that contest, gasoline could be represented by *iso*-octane. Therefore, mixtures of *iso*-octane with alcohols could represent useful surrogates. However, only few studies concern the oxidation/combustion of such blends (Broustail et al. 2011) whereas more studies concerned ethanol-gasoline (Costa and Sodré 2010; Eyidogan et al. 2010; Schifter et al. 2011; Turner et al. 2011) blends and butanol-gasoline blends (Cooney et al. 2009; Dernotte et al. 2010). These experiments did not provide the data needed for detailed kinetic modeling.

As part of a continuing effort in this laboratory to improve the knowledge of fuel combustion kinetics and provide the needed inputs for future modeling, we (i) performed experiments on the oxidation of mixtures of *iso*-octane with ethanol or 1-butanol in a jet-stirred reactor (JSR) and (ii) proposed a kinetic model for representing the data. Iso-octane/alcohols mixtures are interesting for studies in spark ignition engines that normally operate under stoichiometric conditions for optimal pollutants reduction on 3-ways catalysts.

The present experimental and modeling results obtained in the present study are reported in the next sections. They are complementary to those published earlier for the kinetics of oxidation of E85 and Butanol85 where the gasoline fraction was represented by a more complex mixture of *iso*-octane, 1-hexene, and toluene (P. Dagaut and Togbe 2008; P. Dagaut and Togbé 2008).

Experimental

A fused-silica spherical jet-stirred reactor (JSR) operating at 10 atm was used. It is similar to that used previously (P. Dagaut et al. 1986; P. Dagaut and Togbé 2008). It was located inside a regulated electrical resistance oven of ≈1.5kW wrapped with insulating ceramic wool and enclosed in a stainless steel pressure-resistant jacket. Ethanol (99.8% pure, Aldrich), 1-Butanol (99% pure, Aldrich) and *iso*-octane (>99.7% pure, Aldrich) were mixed after thorough ultrasonic degassing. The liquid fuel mixture was pumped, using a micro piston HPLC pump (Shimadzu LC-120 ADvp) with an on-line degasser (Shimadzu DGU-20 A3). It was sent to an in-house stainless steel atomizer-vaporizer assembly maintained at 175 °C. A flow of nitrogen (50L/h) was used for the atomization. The oxygen (99.995% pure, Air Liquide) flow was diluted by a flow of nitrogen (<50 ppm of O_2; <1000 ppm of Ar; <5 ppm of H_2, Air Liquide). This oxygen-nitrogen flow was mixed with the fuel-nitrogen flow just before the entrance of the injectors, after preheating to a temperature close to that inside the JSR. All the gases were regulated by thermal mass-flow controllers (Brooks 5850E). Residence time distribution studies showed that under the conditions of the present study the reactor is operating under macro-mixing conditions (P. Dagaut et al. 1986). As in previous work (P. Dagaut et al. 1986; P. Dagaut and Togbé 2008; Dayma et al. 2007), thermocouple measurements (0.1 mm diameter Pt/ Pt-Rh 10% located inside a thin-wall fused-silica tube to avoid catalytic reactions on the wires) showed good thermal homogeneity along the vertical axis of the reactor. Typical temperature gradients of less than ≈2 K/cm were measured. Since the experiments were performed under high dilution, the temperature rise due to the reaction was generally lower than ≈30 K. Low pressure samples of the reacting mixtures were taken by sonic probe sampling and collected in 1 liter Pyrex bulbs at ≈40 mBar for immediate gas chromatography (GC) analyses as in (P. Dagaut and Togbé 2008; Dayma et al. 2007; Dubreuil et al. 2007).

For the concentration measurements of hydrocarbons and oxygenates, capillary columns of 0.32 mm i.d. (DB-624, 50m and Al_2O_3/KCl 50m) were used with a flame ionization detector (FID) and helium as carrier gas. Hydrogen and oxygen were measured using a 0.53 mm i.d. capillary column (Carboplot, 25m) fitted to a thermal conductivity detector; nitrogen was used as carrier gas. Products identification was made by GC/MS. On-line Fourier transform infra-red (FTIR) analyses of the reacting gases were also performed by connecting the sampling probe to a temperature controlled gas cell (140 °C, 10 m path length, 0.5 cm^{-1} resolution) via a Teflon heated line maintained at 175 °C. The sample pressure in the cell was 0.2 bar. This analytical equipment allowed the measurements of H_2, H_2O, O_2, CO, CO_2, CH_2O, CH_4, C_2H_6, C_2H_4, C_2H_2, ethanol, acetaldehyde, C_3H_6, 1-butanol, butanal, 1- and *iso*-C_4H_8, 1,3-C_4H_6, C_5H_{10}, and *iso*-octane. As previously (P. Dagaut and Togbé 2008; Dayma et al. 2007), very good agreement between the GC and FTIR analyses was found for the compounds measured by both techniques. Carbon balance was checked for every sample and found good (typically 100+/-8%).

Chemical Kinetic Modeling

The chemical kinetic modeling was performed using the PSR computer code of the Chemkin II library (Glarborg et al. 1986). We used a kinetic reaction mechanism (P. Dagaut and Togbé 2008) obtained by merging the oxidation sub-scheme of ethanol and 1-butanol and a more

general hydrocarbon combustion scheme. The resulting scheme (228 species and 1737 reactions) is available from the authors upon request (dagaut@cnrs-orleans.fr). The rate constants for the reverse reactions were computed from the forward rate constants and the appropriate equilibrium constants calculated using thermochemical data (Curran et al. 1998; P. Dagaut and Togbé 2008; Seiser et al. 2000; Tan et al. 1994). This mechanism is limited to high-temperature chemistry because no cool-flame behavior was observed under the conditions of the present work. To rationalize the results, sensitivity analyses and reaction rates analyses were performed. The rates of consumption (R with a negative sign) and production (R with a positive sign) for every species were computed.

Results and Discussion

The oxidation of ethanol-*iso*-octane and 1-butanol-*iso*-octane mixtures (25-75, 50-50, and 75-25 vol. %) was studied. The composition of the reacting mixtures is given in Table 1.

Table 1. Experimental conditions (residence time= 0.7s, pressure= 10 atm, 1500 ppm of fuel, stoichiometic mixtures, balance: nitrogen).

Alcohol-*iso*-octane (vol. %), *mixture*	Initial mole fractions			
	ethanol	1-butanol	*iso*-octane	oxygen
25-75, *A*	0.000728	0	0.000772	0.986664
50-50, *B*	0.001108	0	0.000392	0.008223
75-25, *C*	0.001342	0	0.000158	0.006003
25-75, *D*	0	0.000563	0.000937	0.015089
50-50, *E*	0	0.000965	0.000535	0.012477
75-25, *F*	0	0.001266	0.000234	0.010521

The oxidation of these mixtures was performed in a JSR at a fixed residence time of 0.7 s and at 10 atm. During the JSR experiments, 21 species were identified and measured by GC, FID, and TCD. Experimental mole fractions as a function of temperature were obtained for H_2, H_2O, O_2, CO, CO_2, CH_2O, CH_4, C_2H_6, C_2H_4, C_2H_2, ethanol, acetaldehyde (ethanal), C_3H_6, 1-butanol, butanal, 1- and *iso*-C_4H_8, 1,3-C_4H_6, C_5H_{10} and *iso*-octane. No new species resulting from the interactions of the fuel components or their specific fragments could be measured. No cool flame could be observed in the present experiments in the temperature range 550-800 K, as expected since no such oxidation occurred with the fuel components under similar conditions (P. Dagaut et al. 1994; P. Dagaut and Togbe 2008; P. Dagaut, Sarathy, S. M., Thomson, M. J. 2009; Leplat et al. 2011). The experimental results showed that increasing the initial fraction of alcohol reduces the maximum mole fractions of formaldehyde, methane, and propene, but increases the formation of acetaldehyde and butanal (butanol case only). For ethanol blends, the formation of ethylene decreases with increasing ethanol content in the fuel whereas for butanol blends, the opposite behavior was observed. These trends could be explained using reaction paths analyses, as presented in the next paragraph.

Table 2. Maximum mole fractions of stable intermediates (residence time= 0.7s, pressure= 10 atm, 1500 ppm of fuel, and stoichiometic mixtures).

Alcohol-*iso*-octane (vol. %), *mixture*	Maximum mole fractions					
	CH_2O	CH_3CHO	butanal	CH_4	C_2H_4	C_3H_6
25-75, *A*	2.36E-04	1.42E-04	na	6.31E-04	3.86E-04	1.59E-04
50-50, *B*	1.73E-04	2.02E-04	na	5.18E-04	3.08E-04	8.30E-05
75-25, *C*	1.37E-04	2.36E-04	na	3.61E-04	2.32E-04	3.41E-05

Variation (A to C)	−	+	na	−	−	−
25-75, *D*	3.05E-04	7.36E-05	7.62E-05	6.87E-04	4.95E-04	2.31E-04
50-50, *E*	2.83E-04	9.29E-05	1.16E-04	5.37E-04	5.02E-04	1.98E-04
75-25, *F*	2.61E-04	1.16E-04	1.64E-04	3.92E-04	5.37E-04	1.86E-04
Variation (D to F)	−	+	+	−	+	−

Figures 1 to 6 show comparisons between the present experimental and modeling results using the proposed detailed kinetic scheme. As can be seen from these figures, the model represents well the consumption of the fuels as well as the intermediate formation of hydrocarbons and oxygenates, and that of final products. It should be noted that the intermediate formation of ethylene and methane is generally under-estimated by the model. Also, the maximum mole fraction of carbon monoxide is under-estimated by the model.

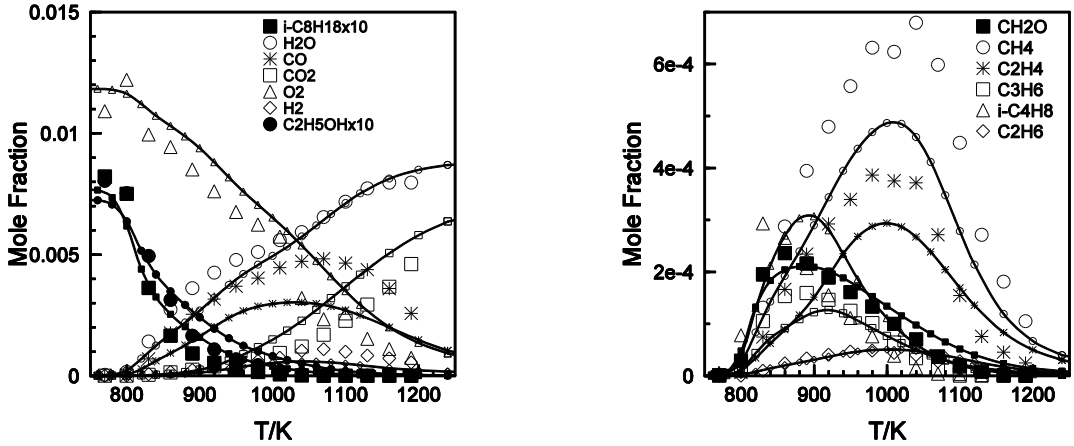

Figure 1. Comparison between experimental (large symbols) and computed (line and small symbol) results for the oxidation of mixture A (ethanol-*iso*-octane 25-75 vol.%) in a JSR.

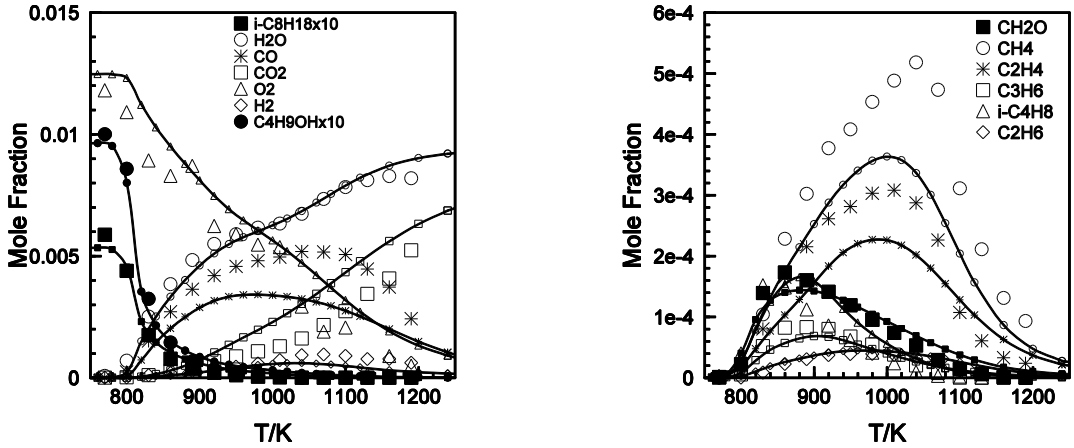

Figure 2. Comparison between experimental (large symbols) and computed (line and small symbol) results for the oxidation of mixture B (ethanol-*iso*-octane 50-50 vol.%) in a JSR.

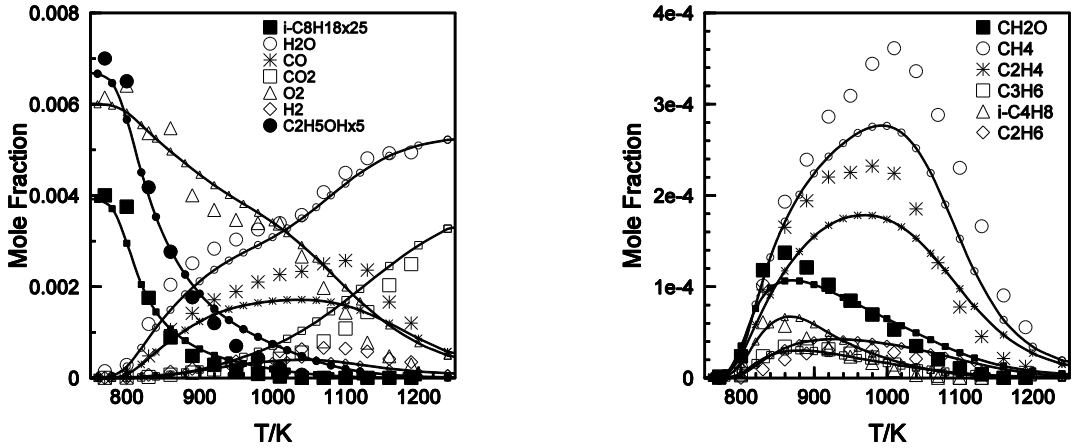

Figure 3. Comparison between experimental (large symbols) and computed (line and small symbol) results for the oxidation of mixture C (ethanol-*iso*-octane 75-25 vol.%) in a JSR.

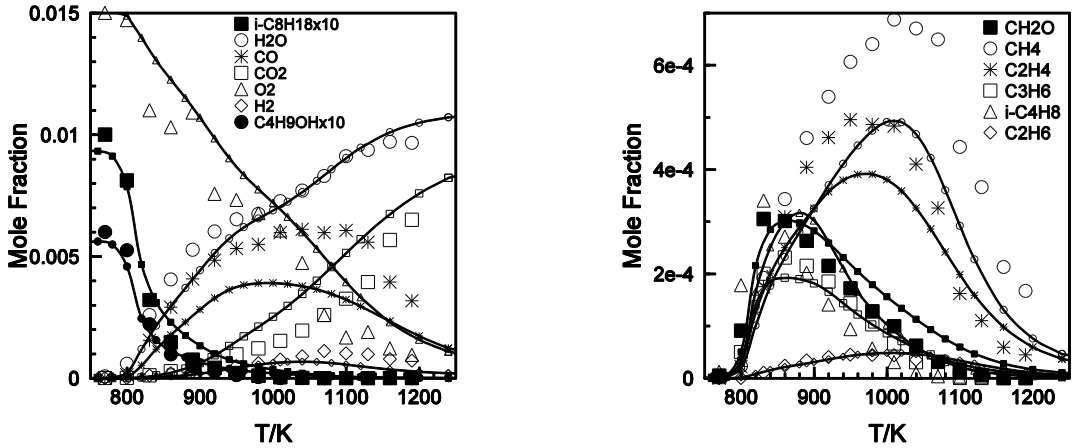

Figure 4. Comparison between experimental (large symbols) and computed (line and small symbol) results for the oxidation of mixture D (butanol-*iso*-octane 25-75 vol.%) in a JSR.

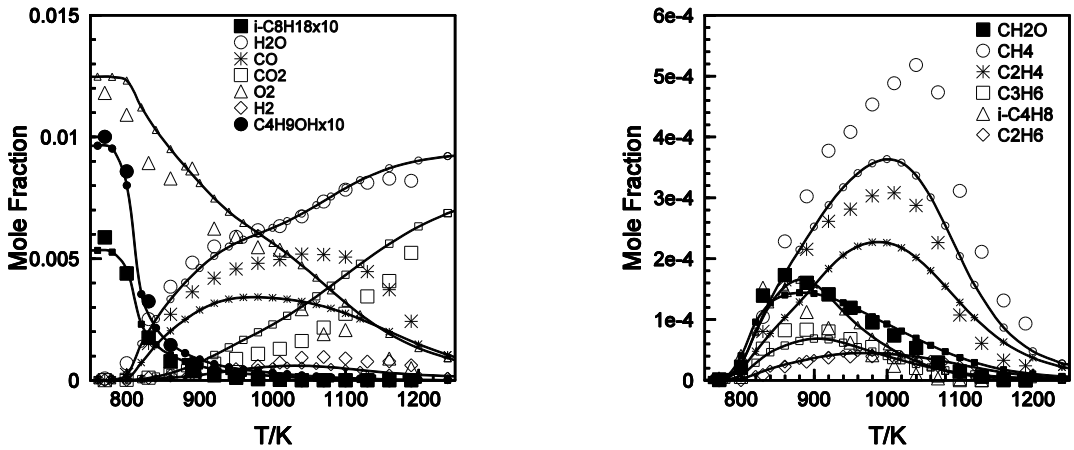

Figure 5. Comparison between experimental (large symbols) and computed (line and small symbol) results for the oxidation of mixture E (butanol-*iso*-octane 50-50 vol.%) in a JSR.

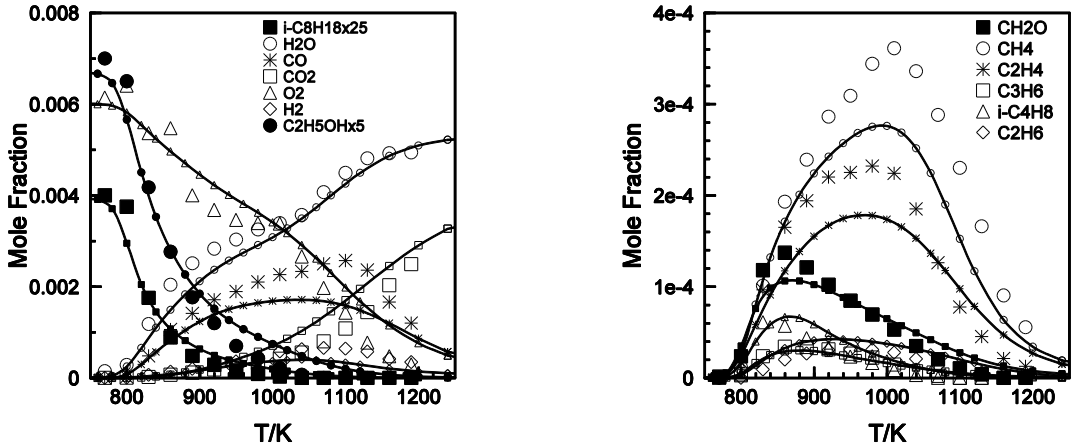

Figure 6. Comparison between experimental (large symbols) and computed (line and small symbol) results for the oxidation of mixture F (butanol-*iso*-octane 75-25 vol.%) in a JSR.

This is due to uncertainties in the *iso*-octane sub-scheme, as demonstrated by modeling the oxidation of pure *iso*-octane under similar conditions (Figure 7). There again, the model under-predicts the formation of ethylene, methane, and carbon monoxide whereas a much better prediction of these species was obtained for the oxidation of butanol and ethanol under similar conditions. Therefore, improving the iso-octane oxidation sub-scheme is still needed. Nevertheless, reaction paths analyses, using the detailed chemical scheme, were performed to delineate the main oxidation reaction paths of the fuels. Normalized rates of production and consumption were computed for every species.

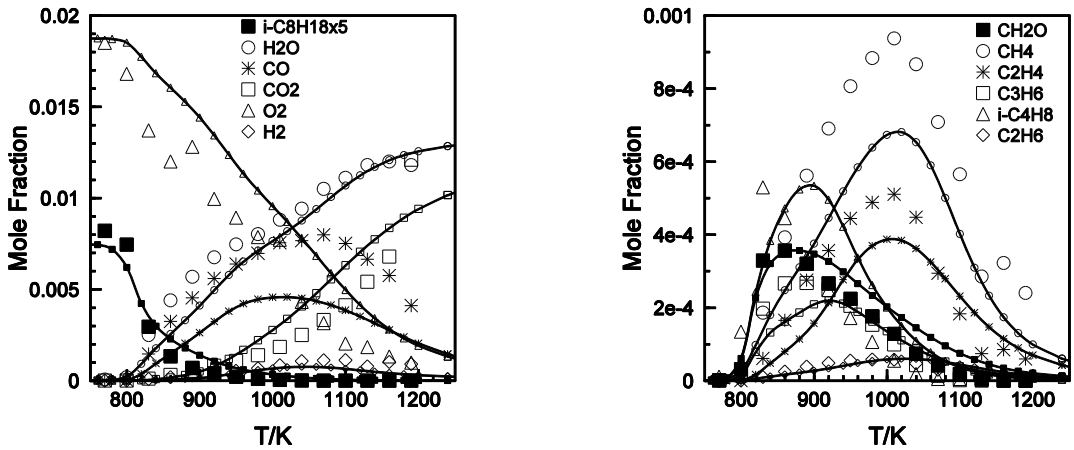

Figure 7. Comparison between experimental (large symbols) and computed (line and small symbol) results for the oxidation of *iso*-octane in a JSR (Mole fractions: *iso*-C_8H_{18}, 0.00150; O_2, 0.01875; N_2, 0.97975; residence time= 0.7s, pressure= 10 atm).

Reaction paths analyses were performed showing that for the ethanol-*iso*-octane fuel mixtures, *iso*-octane reacts predominantly via metathesis with OH (at 900 K, mixture A)

1189. $iC_8H_{18}+OH \rightleftharpoons$ 2,2,4-trimethyl-1-pentyl$+H_2O$; $R(iC_8H_{18})=-0.38$
1190. $iC_8H_{18}+OH \rightleftharpoons$ 2,2,4-trimethyl-3-pentyl$+H_2O$; $R(iC_8H_{18})=-0.17$
1191. $iC_8H_{18}+OH \rightleftharpoons$ 2,4,4-trimethyl-2-pentyl$+H_2O$; $R(iC_8H_{18})=-0.13$
1192. $iC_8H_{18}+OH \rightleftharpoons$ 2,4,4-trimethyl-1-pentyl$+H_2O$; $R(iC_8H_{18})=-0.14$

Ethanol is also mainly consumed via reaction with OH

1543. $C_2H_5OH+OH \rightleftarrows C_2H_4OH+H_2O$; R(ethanol)=-0.11
1544. $C_2H_5OH+OH \rightleftarrows CH_3CHOH+H_2O$; R(ethanol)=-0.69
1545. $C_2H_5OH+OH \rightleftarrows CH_3CH_2O+H_2O$; R(ethanol)=-0.04

Increasing the initial fraction of ethanol reduces the maximum mole fractions of formaldehyde because its formation by decomposition of C_4H_7O and reaction of iC_8H_{15} with O_2 get less important and slower.

1161. $C_4H_7O \rightleftarrows tC_3H_5+CH_2O$
1323. $IC_8H_{15}+O_2 \rightarrow$ acetone$+iC_4H_7+CH_2O$

The rate of reaction 1161 is reduced by a factor of ≈4 and that of reaction 1323 by a factor of ≈11 when moving from mixture A to mixture C. Increasing the initial fraction of ethanol reduces the maximum mole fractions of methane because of the reduced rate of production of methyl radical (10% reduction), itself resulting from a lower concentration of *iso*-octane. Methane is mainly produced by reactions of methyl radicals with HO_2, CH_2O, iC_4H_8, and the fuel components. Increasing the initial fraction of ethanol reduces the maximum mole fractions of propene because propene production mostly results from the oxidation of *iso*-octane (at 900 K, mixture C):

289. $iC_3H_7+O_2 \rightleftarrows C_3H_6+HO_2$; R(propene)=0.3
1072. $iC_4H_9 \rightleftarrows C_3H_6+CH_3$; R(propene)=0.08
1097. $iC_4H_8+H \rightleftarrows C_3H_6+CH_3$; R(propene)=0.22
1233. 4,4-dimethyl-2-pentyl $\rightleftarrows C_3H_6+TC_4H_9$; R(propene)=0.148
1281. 2,4,4-trimethyl-1-pentyl $\rightleftarrows neoC_5H_{11}+C_3H_6$; R(propene)=0.078

Increasing the initial fraction of ethanol increases the maximum mole fractions of acetaldehyde because ethanol readily produces acetaldehyde, as already reported (P. Dagaut and Togbe 2008) (at 900 K, mixture C):

1565. $CH_3CHOH+O_2 \rightleftarrows CH_3HCO+HO_2$; R($CH_3HCO$)=0. 9
1570. $CH_3CHOH+HO_2 \rightleftarrows CH_3HCO+2OH$; R($CH_3HCO$)=0.04
1572. $CH_3CHOH+M \rightleftarrows CH_3HCO+H+M$; R($CH_3HCO$)=0.04

Increasing the initial fraction of ethanol decreases the maximum mole fractions of ethylene because ethanol produces very little ethylene by oxidation. Its formation occurs via

1589. $nC_3H_7(+M) \rightleftarrows C_2H_4+CH_3(+M)$
1603. $C_2H_5+O_2 \rightleftarrows C_2H_4+HO_2$

Reaction paths analyses were performed showing that for the butanol-*iso*-octane fuel mixtures, *iso*-octane reacts predominantly via metathesis with OH, as already described for the ethanol-*iso*-octane mixtures. Butanol is mainly consumed via metathesis with OH:

1648. $C_4H_9OH+OH \rightarrow H_2O+1C_4H_8OH$
1649. $C_4H_9OH+OH \rightarrow H_2O+C_4H_9O$

1650. $C_4H_9OH+OH \rightarrow H_2O+4C_4H_8OH$
1651. $C_4H_9OH+OH \rightarrow H_2O+3C_4H_8OH$
1652. $C_4H_9OH+OH \rightarrow H_2O+2C_4H_8OH$

Increasing the initial fraction of butanol increases the maximum mole fractions of butanal because it is essentially formed by oxidation of butanol:

1622. $C_4H_9O \rightarrow H+C_3H_7CHO$
1633. $1C_4H_8OH+O_2 \rightarrow C_3H_7CHO+HO_2$
1634. $C_4H_9O+O_2 \rightarrow C_3H_7CHO+HO_2$

Increasing the initial fraction of butanol reduces the maximum mole fractions of formaldehyde for the same reasons as with the ethanol-*iso*-octane fuel mixture. Increasing the initial fraction of butanol reduces the maximum mole fractions of methane because of the reduced rate of production of methyl radical, itself resulting from a reduced concentration of *iso*-octane. Increasing the initial fraction of butanol reduces the maximum mole fractions of propene because of the reduced rate of production of *iso*propyl radicals through *iso*-octane oxidation, although propene is also produced by butanol oxidation:

289. $iC_3H_7+O_2 \rightleftarrows C_3H_6+HO_2$
1624. $3C_4H_8OH \rightarrow CH_2OH+C_3H_6$

Increasing the initial fraction of butanol (mixture D to F) increases the maximum mole fractions of ethylene as a result of the increased rates of reactions 1589 and 1603 by a factor of ≈2:

1589. $nC_3H_7(+M) \rightleftarrows C_2H_4+CH_3(+M)$
1603. $C_2H_5+O_2 \rightleftarrows C_2H_4+HO_2$

Local, first-order sensitivity analyses were performed to delineate the most influencing reactions in the scheme. Reaction presenting positive sensitivity coefficients will reduce the conversion rate of iso-octane if their kinetics is increased. Conversely, reactions presenting negative sensitivity coefficients will accelerate the conversion of iso-octane if their kinetics is increased.

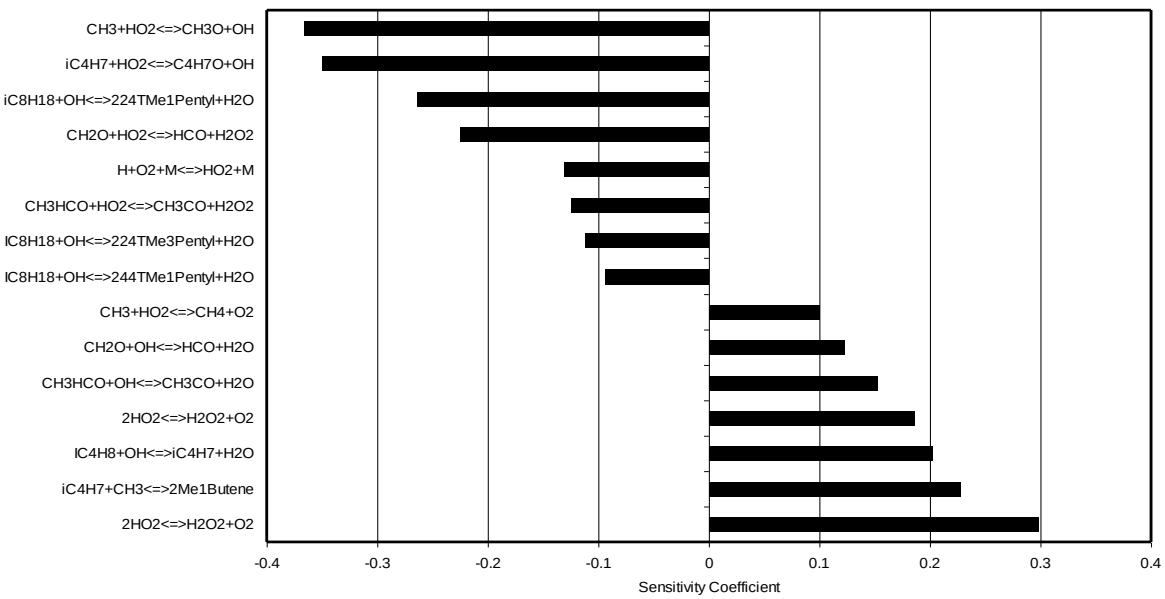

Figure 8. Sensitivity spectrum for *iso*-octane (Mixture B ethanol/*iso*-octane at 900 K, 10 atm, 0.7s). The reaction 2 $HO_2 \rightleftarrows H_2O_2+O_2$ appears twice because its complex temperature dependence required using two Arrhenius expressions.

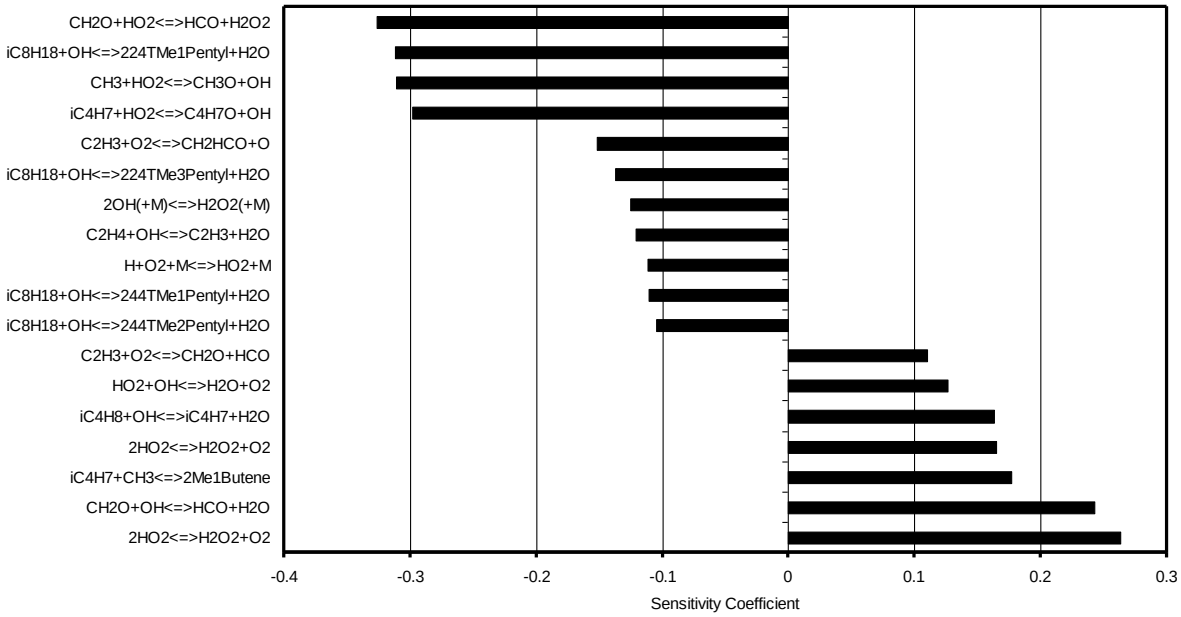

Figure 9. Sensitivity spectrum for *iso*-octane (Mixture E butanol/*iso*-octane at 900 K, 10 atm, 0.7s). The reaction 2 $HO_2 \rightleftarrows H_2O_2+O_2$ appears twice because its complex temperature dependence required using two Arrhenius expressions.

As can be seen from Figures 8-9, the most sensitive reactions remain the same when ethanol or butanol is present in the fuel mixture. From Figure 8, it can be seen that *iso*-octane oxidation is favored by reactions producing OH radicals

45. $CH_3+HO_2 \rightleftarrows CH_3O+OH$
1104. $iC_4H_7+HO_2 \rightleftarrows C_4H_7O+OH$

that are mostly responsible for iso-octane consumption.

1190. $IC_8H_{18}+OH \rightleftarrows$ 2,2,4-trimethyl-3-pentyl$+H_2O$
1192. $IC_8H_{18}+OH \rightleftarrows$ 2,4,4-trimethyl-1-pentyl$+H_2O$

Furthermore, reactions producing HO_2 radicals (7. $H+O_2+M \rightleftarrows HO_2+M$) also favor the oxidation of iso-octane through the further conversion of HO_2 into OH radicals via reactions 45 and 1104. Other reaction consuming OH and/or HO_2 radicals tend to reduce the rate of oxidation of iso-octane under these conditions. The kinetics of reactions pertaining to the ethanol sub-scheme also influences the model predictions since the following reactions have significant sensitivity coefficients:

249. $CH_3HCO+OH \rightleftarrows CH_3CO+H_2O$
248. $CH_3HCO+HO_2 \rightleftarrows CH_3CO+H_2O_2$

By consuming OH radicals, reaction tends to reduce the rate of consumption of the fuel that mostly reacts with OH. Conversely, reaction 248 that produces H_2O_2 tends to favor the oxidation of the fuel since in turn, hydrogen peroxide decomposes to yield two OH radicals.

For the oxidation of the iso-octane-butanol mixture E under the same conditions (Figure 9), one can see that again *iso*-octane oxidation is favored by reactions producing OH radicals

45. $CH_3+HO_2 <=> CH_3O+OH$,
1104. $iC_4H_7+HO_2 <=> C_4H_7O+OH$

the main radical responsible for the oxidation of iso-octane:

1189. $iC_8H_{18}+OH \rightleftarrows$ 2,2,4-trimethyl-1-pentyl$+H_2O$
1190. $iC_8H_{18}+OH \rightleftarrows$ 2,2,4- trimethyl-3-pentyl$+H_2O$
1191. $iC_8H_{18}+OH \rightleftarrows$ 2,4,4- trimethyl-2-pentyl$+H_2O$
1192. $iC_8H_{18}+OH \rightleftarrows$ 2,4,4- trimethyl-1-pentyl$+H_2O$

Conversely, reaction consuming OH and/or HO_2 radicals tend to reduce the rate of oxidation of iso-octane under these conditions:

11. $HO_2+OH \rightleftarrows H_2O+O_2$
16 and 17. $2HO_2 \rightleftarrows H_2O_2+O_2$
113. $CH_2O+OH \rightleftarrows HCO+H_2O$
1092. $iC_4H_8+OH \rightleftarrows iC_4H_7+H_2O$

Conclusion

The two main objectives of this study were achieved: (i) New data consisting of concentration profiles of reactants, stable intermediates, and final products were measured as a function of temperature for the oxidation of stoichiometric mixtures of ethanol and *iso*-octane and 1-butanol and *iso*-octane, in a JSR operating at 10 atm and 0.7s; (ii) A chemical kinetic modeling of these experiments was performed using a mechanism derived from previous work. Very similar reaction paths were observed when increasing the alcohol fraction in the fuel (25 to 75% vol.). As expected, increasing the initial fraction of alcohol in the fuel increases the importance of its reaction routes for the formation of the products measured here. Variations in products formation with changing fuel composition were rationalized through kinetic modeling.

References

Barker, T., Bashmakov, I., Bernstein, L., Bogner, J. E., Bosch, P. R., Dave, R., Davidson, O. R., Fisher, B. S., Gupta, S., Halsnæs, K., Heij, G.J., Kahn Ribeiro, S. Kobayashi, S., Levine, M. D., Martino, D. L., Masera, O., Metz, B., Meyer, L. A., Nabuurs, G.-J., Najam, A., Nakicenovic, N., Rogner, H. -H., Roy, J., Sathaye, J., Schock, R., Shukla, P., Sims, R. E. H., Smith, P., Tirpak, D. A., Urge-Vorsatz, D., Zhou, D. (2007), *Technical Summary. In: Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, ed. O. R. Davidson B. Metz, P. R. Bosch, R. Dave, L. A. Meyer (Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA).

BP and Dupont <http://www.bp.com/liveassets/bp_internet/globalbp/STAGING/global_assets/downloads/B/Bio_bp_dupont_fact_sheet_jun06.pdf>.

Broustail, G., Seers, P., Halter, F., Moréac, G., and Mounaim-Rousselle, C. (2011) Experimental determination of laminar burning velocity for butanol and ethanol iso-octane blends. *Fuel,* 90 (1), 1-6.

Cooney, C., Wallner, T., McConnell, S., Gillen, J. C., Abell, C., Miers, S. A., Naber, J. D., and asme (2009), *Effects of blending gasoline with ethanol and butanol on engine efficiency and emissions using a direct-injection, spark-ignition engine* (Proceedings of the 2009 Spring Technical Conference of the Asme Internal Combustion Engine Division) 157-65.

Costa, Rodrigo C. and Sodré, José R. (2010) Hydrous ethanol vs. gasoline-ethanol blend: Engine performance and emissions. *Fuel,* 89 (2), 287-93.

Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K. (1998) A comprehensive modeling study of n-heptane oxidation. *Combustion and Flame,* 114 (1-2), 149-77.

Dagaut, P. and Togbé, C. (2008) Oxidation kinetics of butanol-gasoline surrogate mixtures in a jet-stirred reactor: Experimental and modeling study. *Fuel,* 87 (15-16), 3313-21.

Dagaut, P. and Togbe, C. (2008) Experimental and modeling study of the kinetics of oxidation of ethanol-gasoline surrogate mixtures (E85 surrogate) in a jet-stirred reactor. *Energy & Fuels,* 22 (5), 3499-505.

Dagaut, P., Reuillon, M., and Cathonnet, M. (1994) High-Pressure Oxidation of Liquid Fuels from Low to High-Temperature .1. N-Heptane and Isooctane. *Combustion Science and Technology,* 95 (1-6), 233-60.

Dagaut, P., Cathonnet, M., Rouan, J. P., Foulatier, R., Quilgars, A., Boettner, J. C., Gaillard, F., and James, H. (1986) A Jet-Stirred Reactor for Kinetic-Studies of Homogeneous Gas-Phase Reactions at Pressures up to 10-Atmospheres (~ 1 MPa). *Journal of Physics E-Scientific Instruments,* 19 (3), 207-09.

Dagaut, P., Sarathy, S. M., Thomson, M. J. (2009) A Chemical Kinetic Study of n-Butanol Oxidation at Elevated Pressure in a Jet Stirred Reactor. *Proceedings of the combustion Institute,* 32, 229-37.

Dayma, G., Hadj Ali, K., and Dagaut, P. (2007) Experimental and detailed kinetic modeling study of the high pressure oxidation of methanol sensitized by nitric oxide and nitrogen dioxide. *Proceedings of the Combustion Institute,* 31 (1), 411-18.

Dernotte, J., Mounaim-Rousselle, C., Halter, F., and Seers, P. (2010) Evaluation of Butanol-Gasoline Blends in a Port Fuel-injection, Spark-Ignition Engine. *Oil & Gas Science and Technology-Revue De L Institut Francais Du Petrole,* 65 (2), 345-51.

Dubreuil, Anthony, Foucher, Fabrice, Mounaim-Rousselle, Christine, Dayma, Guillaume, and Dagaut, Philippe (2007) HCCI combustion: Effect of NO in EGR. *Proceedings of the Combustion Institute,* 31 (2), 2879-86.

Eyidogan, Muharrem, Ozsezen, Ahmet Necati, Canakci, Mustafa, and Turkcan, Ali (2010) Impact of alcohol-gasoline fuel blends on the performance and combustion characteristics of an SI engine. *Fuel,* 89 (10), 2713-20.

Ezeji, Thaddeus Chukwuemeka, Qureshi, Nasib, and Blaschek, Hans Peter (2007) Bioproduction of butanol from biomass: from genes to bioreactors. *Current Opinion in Biotechnology,* 18 (3), 220-27.

Farrell, A. E., Plevin, R. J., Turner, B. T., Jones, A. D., O'Hare, M., and Kammen, D. M. (2006) Ethanol can contribute to energy and environmental goals. *Science,* 311 (5760), 506-08.

Fontaras, G. and Samaras, Z. (2007) A quantitative analysis of the European Automakers' voluntary commitment to reduce CO2 emissions from new passenger cars based on independent experimental data. *Energy Policy,* 35 (4), 2239-48.

Glarborg, P., Kee, R.J., Grcar, J.F., and Miller, J.A. (1986). PSR: A FORTRAN program for modeling well-stirred reactors, *SAND86-8209* (Livermore, CA: Sandia National Laboratories).

Gorham, R. (2002). Air pollution from ground transportation an assessment of causes, strategies and tactics, and proposed actions for the international community, (United Nations, Department of Economic and Social Affairs, Division for Sustainable Development).

Iliuc, I. (2008) EU objective of 120g CO2/km emission for new cars, a challenge for tribology. *Mathematics and Computers in Biology and Chemistry*, 66-71.

Jacobson, M. Z. (2007) Effects of ethanol (E85) versus gasoline vehicles on cancer and mortality in the United States. *Environmental Science & Technology,* 41 (11), 4150-57.

Kim, S. and Dale, B. E. (2006) Ethanol fuels: E10 or E85 - Life cycle perspectives. *International Journal of Life Cycle Assessment,* 11 (2), 117-21.

Leplat, N., Dagaut, P., Togbe, C., and Vandooren, J. (2011) Numerical and experimental study of ethanol combustion and oxidation in laminar premixed flames and in jet-stirred reactor. *Combustion and Flame,* 158 (4), 705-25.

Low, S. A. and Isserman, A. M. (2009) Ethanol and the Local Economy Industry Trends, Location Factors, Economic Impacts, and Risks. *Economic Development Quarterly,* 23 (1), 71-88.

Magnusson, R., Nilsson, C., and Andersson, B. (2002) Emissions of aldehydes and ketones from a two-stroke engine using ethanol and ethanol-blended gasoline as fuel. *Environmental Science & Technology,* 36 (8), 1656-64.

Niven, R. K. (2005) Ethanol in gasoline: environmental impacts and sustainability review article. *Renewable & Sustainable Energy Reviews*, 9 (6), 535-55.

Qureshi, Nasibuddin and Maddox, Ian S. (1995) Continuous production of acetone-butanol-ethanol using immobilized cells of Clostridium acetobutylicum and integration with product removal by liquid-liquid extraction. *Journal of Fermentation and Bioengineering*, 80 (2), 185-89.

Schifter, I., Diaz, L., Rodriguez, R., Gómez, J. P., and Gonzalez, U. (2011) Combustion and emissions behavior for ethanol-gasoline blends in a single cylinder engine. *Fuel*, DOI: 10.1016/j.fuel.2011.01.034.

Seiser, R., Pitsch, H., Seshadri, K., Pitz, W. J., and Curran, H. J. (2000) Extinction and autoignition of n-heptane in counterflow configuration. *Proceedings of the Combustion Institute*, 28, 2029-37.

Singh, A., Gangopadhyay, S., Nanda, P. K., Bhattacharya, S., Sharma, C., and Bhan, C. (2008) Trends of greenhouse gas emissions from the road transport sector in India. *Science of the Total Environment*, 390 (1), 124-31.

Tan, Y. , Dagaut, P., Cathonnet, M., and Boettner, J. C. (1994) Acetylene Oxidation in a JSR from 1-Atm to 10-Atm and Comprehensive Kinetic Modeling. *Combustion Science and Technology*, 102 (1-6), 21-55.

Tashiro, Yukihiro, Takeda, Katsuhisa, Kobayashi, Genta, and Sonomoto, Kenji (2005) High production of acetone-butanol-ethanol with high cell density culture by cell-recycling and bleeding. *Journal of Biotechnology*, 120 (2), 197-206.

Tashiro, Yukihiro, Shinto, Hideaki, Hayashi, Miki, Baba, Shun-ichi, Kobayashi, Genta, and Sonomoto, Kenji (2007) Novel high-efficient butanol production from butyrate by non-growing Clostridium saccharoperbutylacetonicum N1-4 (ATCC 13564) with methyl viologen. *Journal of Bioscience and Bioengineering*, 104 (3), 238-40.

Turner, Dale, Xu, Hongming, Cracknell, Roger F., Natarajan, Vinod, and Chen, Xiangdong (2011) Combustion performance of bio-ethanol at various blend ratios in a gasoline direct injection engine. *Fuel*, 90 (5), 1999-2006.

von Blottnitz, H. and Curran, M. A. (2007) A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective. *Journal of Cleaner Production*, 15 (7), 607-19.

Winebrake, J. J., Wang, M. Q., and He, D. Q. (2001) Toxic emissions from mobile sources: A total fuel-cycle analysis for conventional and alternative fuel vehicles. *Journal of the Air & Waste Management Association*, 51 (7), 1073-86.