

# COMBUSTION OF BIO- AND BIOMASS-DERIVED FUELS TO ADDRESS SECURITY OF SUPPLY AND EFFICIENCY CHALLENGES: A CHEMICAL KINETIC PROSPECTIVE



Philippe Dagaut

*Centre National de la Recherche Scientifique*

*1C, Ave de la Recherche Scientifique - 45071 Orléans Cedex 2 – France*



# Motivations

Biomass derived fuels are generally considered sustainable alternatives to fossil fuels

**Gaseous fuels** derived from biomass can be used in **conventional and new combustion devices.**

Among them, hydrogen and syngas (CO/H<sub>2</sub>) can be used in various amounts with natural gas.

# Motivations

'**Flameless combustion**' is an interesting emerging combustion concept that can be used for **reducing pollutant emissions** [[Cavaliere, de Joannon, \*Prog. Energy Combust. Sci.\* \*\*30\*\*, 329–366, 2004](#)], particularly NO<sub>x</sub>, and **improve combustion efficiency**.

Its application to gas turbine is currently studied [[Flamme, \*Appl. Therm. Eng.\* \*\*24\*\*, 551-1559, 2004](#); [Levy et al., \*Appl. Therm. Eng.\*, \*\*24\*\*, 1593-1605, 2004, etc.](#)].

In this type of combustor, the **reactants are preheated** and **diluted by exhaust gases**, mainly **H<sub>2</sub>O**, **CO<sub>2</sub>**, CO, and traces of **NO<sub>x</sub>**.

# Motivations

'**Flameless combustion**' is an interesting emerging combustion concept that can be used for **reducing pollutant emissions** [Cavaliere, de Joannon, *Prog. Energy Combust. Sci.* **30**, 329–366, 2004], particularly  $\text{NO}_x$ , and **improve combustion efficiency**.

Its application to gas turbine is currently studied [Flamme, *Appl. Therm. Eng.* **24**, 551-1559, 2004; Levy et al., *Appl. Therm. Eng.*, **24**, 1593-1605, 2004, etc.].

In this type of combustor, the **reactants are preheated and diluted by exhaust gases**, mainly  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and traces of  $\text{NO}_x$ .

Also, in gas turbines,  $\text{H}_2\text{O}$  is injected to limit  $\text{NO}_x$  formation [Skevis et al., 2004, *Appl. Therm. Eng.* **24**, 1607-1618; De Jager et al., 2007, *Proc. Combust. Inst.* **31**, 3123-3130; Jonsson, Yan, 2005, *Energy* **30**, 1013-1078].

**Therefore, it is important to study the effect of such compounds on the kinetics of oxidation of conventional fuels (NG) or non-conventional fuels ( $\text{CO}/\text{H}_2/\dots$ ).**

The effect of  $\text{NO}_x$  and  $\text{CO}_2$  recirculation was previously addressed in part [Dagaut, Nicolle 2005, *Combust. Flame* **140**, 161-171; Dagaut et al. 2005, *Combust. Sci. and Technol.* **177**, 1767-1791; Nicolle, Dagaut, 2006, *Fuel* **85**, 2469-2478; Le Cong et al., 2008, *J. Eng. Gas Turbines and Power*, **130**, 041502-1,10] whereas that of  $\text{H}_2\text{O}$  was not until recently [Le Cong and Dagaut, *Energy & Fuels* **23**, 2009].

## Motivations

**Alcohols** obtained from biomass fermentation can be used as fuels for ground transportation, and more? Among them, ethanol and n-butanol represent interesting alternatives to petrol-derived liquid fuels, although several environmental issues need to be addressed.

**Methyl esters** derived from vegetable oil or animal fat (FAME) are already used in 'Bio-Diesel'. More about their combustion chemistry needs to be known.

# Introduction: Gaseous fuels

Recently, **new experimental results** were obtained **for the neat oxidation of hydrogen and methane** in a JSR at 1 atm, over a wide range of equivalence ratio (0.1 to 1.5), for temperatures in the range 800-1500 K.

Corresponding experiments where **10% H<sub>2</sub>O** (in mole) is present in the reacting mixtures were also performed

**The oxidation of hydrogen in presence of 30% CO<sub>2</sub>** in a JSR at 1 atm, over a range of equivalence ratio (0.2 to 2), and for temperatures in the range 800-1050 K and experiments where **different concentrations of H<sub>2</sub> are added to methane and methane-20% CO<sub>2</sub> mixtures** were also performed at 1 and 10 atm.

# Introduction: Gaseous fuels

Recently, **new experimental results** were obtained **for the neat oxidation of hydrogen and methane** in a JSR at 1 atm, over a wide range of equivalence ratio (0.1 to 1.5), for temperatures in the range 800-1500 K.

Corresponding experiments where **10% H<sub>2</sub>O** (in mole) is present in the reacting mixtures were also performed.

**The oxidation of hydrogen in presence of 30% CO<sub>2</sub>** in a JSR at 1 atm, over a range of equivalence ratio (0.2 to 2), and for temperatures in the range 800-1050 K and experiments where **different concentrations of H<sub>2</sub> are added to methane and methane-20% CO<sub>2</sub> mixtures** were also performed at 1 and 10 atm.

**Comprehensive model validation:** The oxidation of these fuels under JSR, shock-tube and premixed flame conditions is modeled.

Kinetic analyses including sensitivity analyses and reaction path analyses are used to rationalize the results.

# Introduction: Liquid fuels

We intended to provide the needed combustion modeling inputs by

(i) **performing experiments** on the oxidation of alcohols(methanol, ethanol, 1-butanol), alcohol-fuel surrogate mixtures, methyl esters, and FAME in a jet-stirred reactor (JSR)

and

(ii) **proposing kinetic models** representing the data, where **surrogate fuels** are used,

# Introduction: Liquid fuels

This 'surrogate-fuel' and/or 'model-fuel' approach follows that previously used for representing the combustion of

a **gasoline**, [M. Yahyaoui et al., *Proc. Combust. Inst.* **2007**, 31, 385-391]

a **diesel fuel**, Mati et al., *Proc. Combust. Inst.* **2007**, 31, (2), 2939-2946

a **jet fuel** [Dagaut et al., *Fuel* **2006**, 85, (7-8), 944-956],

a "**biokerosene**" i.e. Jet-A1/RME [Dagaut and Gail, *J. Phys. Chem. A* **2007**, 111, (19), 3992-4000], and

a "**biodiesel**" i.e. RME [Dagaut et al., *Proc. Combust. Inst.* **2007**, 31, (2), 2955-2961]

with a **limited** number of constituents.

# Experimental

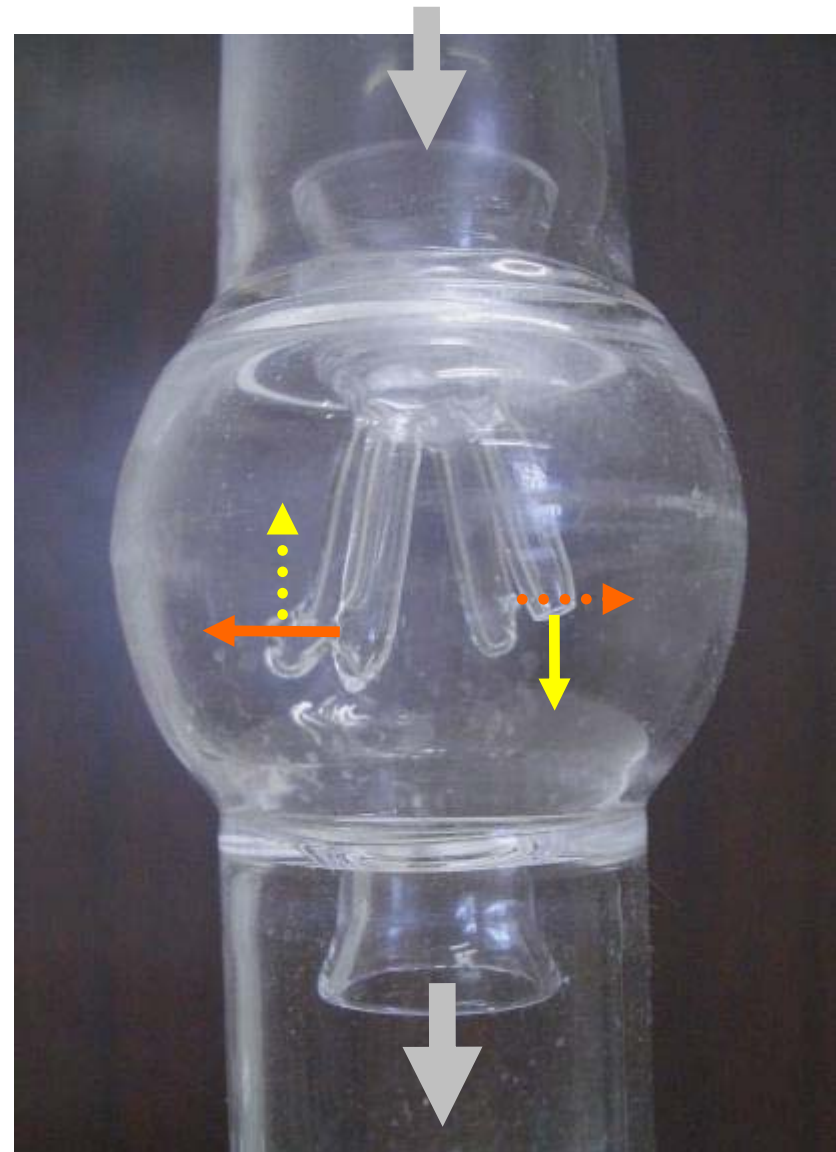
- A fused silica **jet-stirred reactor** (c.a. 30 cm<sup>3</sup>): 4 injectors (nozzles of 1 mm i.d.), located inside a regulated electrical oven of 1.5kW.

Flow rates of **Fuel, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>** regulated by thermal mass-flow controllers. The fuels and O<sub>2</sub> are diluted by N<sub>2</sub>. They flow separately; they are mixed at the entrance of the injectors after preheating.

- **Macro-mixing conditions** achieved: A PSR model is usable.

- **Thermal homogeneity** checked/TC (Pt/Pt-Rh10%, 0.1mm) < 8K.

- High-purity reactants were used: O<sub>2</sub> (99.995% pure), methane (99.9995% pure), hydrogen (99.995% pure)

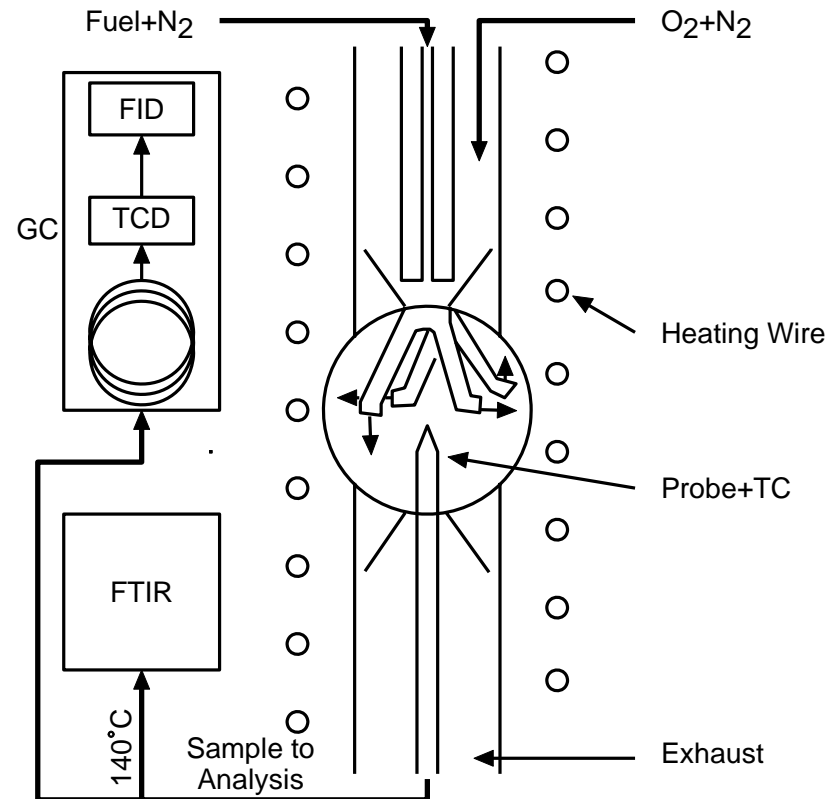


# Experimental

- Low-P samples taken by sonic probe sampling for **GC analyses** (Capillary columns of 0.53 mm i.d. - Poraplot U and Molecular sieve 5A- were used with **TCD-FID**).

- On-line **FTIR, GC-MS analyses**

- C-balance checked for every sample and found good (100+/-10%).



# Modeling

For simulating the oxidation of the fuels in premixed flames, we used the **PREMIX** computer code.

For simulating the ignition delays in air, we used the **SENKIN** code.

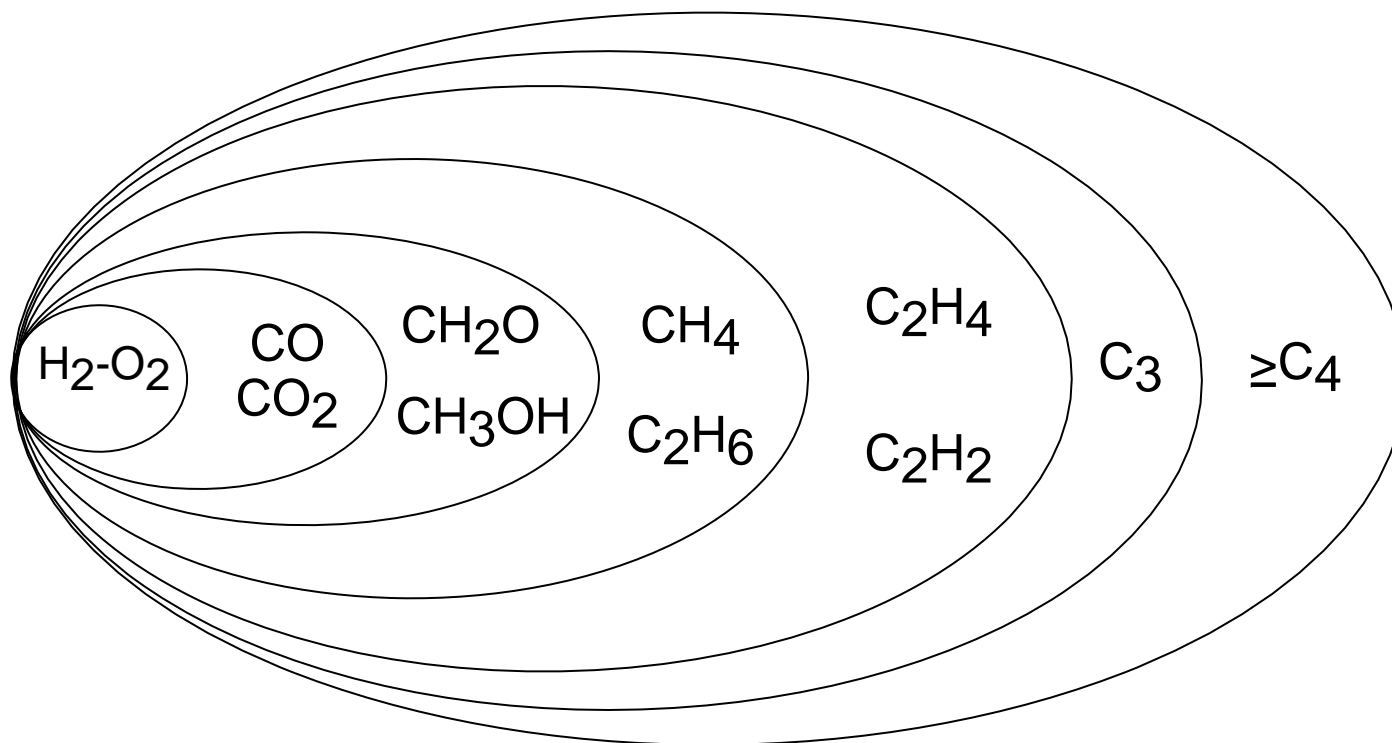
For the JSR computations, we used the **PSR** computer code.

The reaction rates are computed from the kinetic reaction mechanism and the rate constants of the elementary reactions calculated using the modified Arrhenius equation:

$$k = A \cdot T^n \cdot \exp(-E/RT)$$

# Modeling

The **kinetic scheme** is based on the comprehensive hydrocarbon oxidation mechanism developed earlier for NG to Diesel [[Dagaut, \*Phys. Chem. Chem. Phys.\* 4, 2079-2094, 2002 and updates](#)].



The kinetic reaction mechanism has a strong hierarchical structure.

# I. Gaseous fuels oxidation

# RESULTS

A large set of experimental results was obtained for the JSR oxidation of

**hydrogen**

**methane**

**hydrogen-methane** fuel mixtures

over the temperature range 800-1500 K,

for equivalence ratios ranging from 0.1 to 2,

for various mole fractions of methane, hydrogen, **carbon dioxide**, and **water vapor**.

The experiments were performed at constant mean residence time

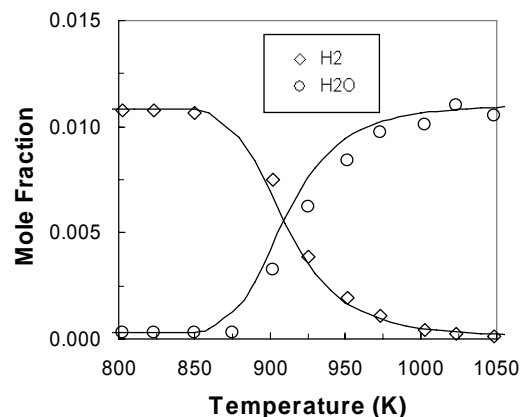
The reaction was studied by varying stepwise the operating temperature in the JSR.

Measurements of concentration profiles for the reactants, stable intermediates, and final products: O<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>.

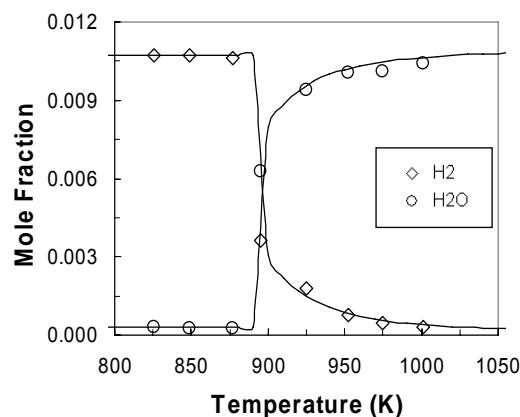
The proposed kinetic reaction mechanism was used to simulate these experiments.

# Hydrogen and Hydrogen-H<sub>2</sub>O oxidation

# Hydrogen oxidation

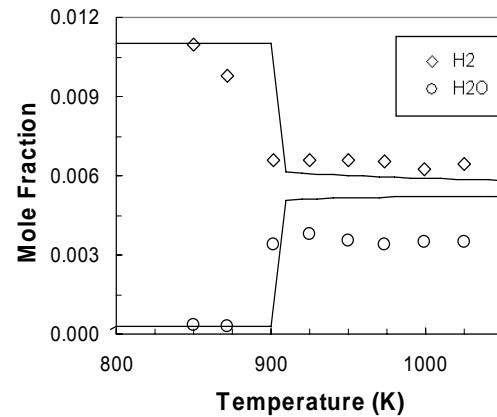


The oxidation of hydrogen in a JSR (1 atm,  $\tau=120$  ms, 1% H<sub>2</sub>,  $\phi=0.2$ , dilution by nitrogen). The data (large symbols) are compared to the modeling (lines and small symbols).



The oxidation of hydrogen in a JSR (1 atm,  $\tau=120$  ms, 1% H<sub>2</sub>,  $\phi=0.5$ , dilution by nitrogen). The data (large symbols) are compared to the modeling (lines and small symbols).

# Hydrogen oxidation

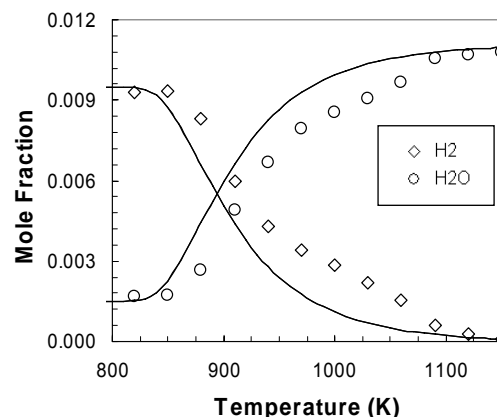


The oxidation of hydrogen in a JSR (1 atm,  $\tau=120$  ms, 1% H<sub>2</sub>,  $\phi=2$ , dilution by nitrogen). The data (large symbols) are compared to the modeling (lines and small symbols).

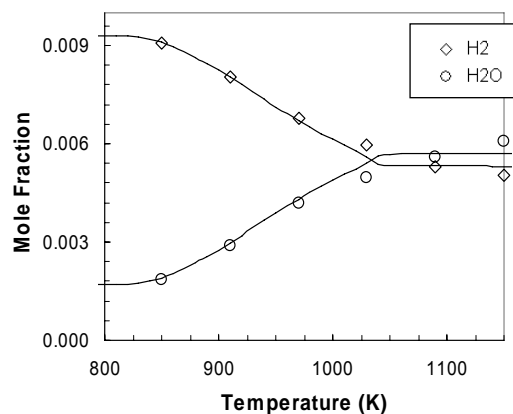
The model represents fairly well this new data set for the oxidation of hydrogen.

The model also represents fairly well a former data set for the oxidation of hydrogen [Dayma, Dagaut, 2006, *Int. J. Hydrogen Energy* **31**, 505-515.]: *next slide*

# Hydrogen oxidation

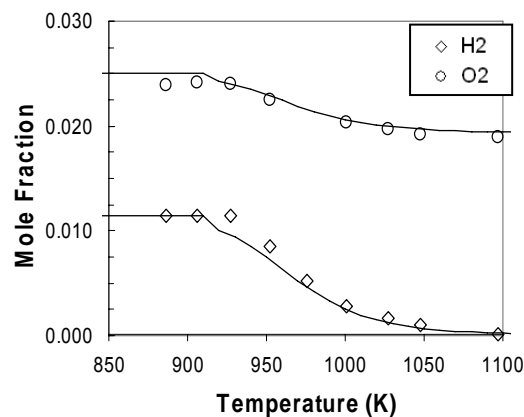


The oxidation of hydrogen in a JSR (10 atm,  $\tau=1000$  ms, 1% H<sub>2</sub>,  $\phi=0.1$ , dilution by nitrogen). The data (large symbols) are compared to the modeling (lines and small symbols).

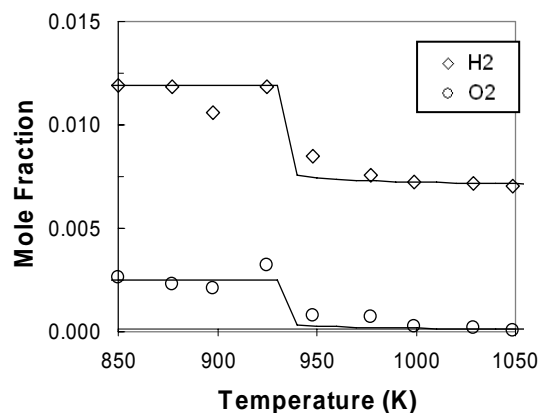


The oxidation of hydrogen in a JSR (10 atm,  $\tau=1000$  ms, 1% H<sub>2</sub>,  $\phi=2.5$ , dilution by nitrogen). The data (large symbols) are compared to the modeling (lines and small symbols).

# Hydrogen-H<sub>2</sub>O oxidation



The oxidation of hydrogen in a JSR (1 atm,  $\tau=120$  ms, 1% H<sub>2</sub>,  $\phi=0.2$ , dilution by nitrogen, 10% H<sub>2</sub>O). The data (large symbols) are compared to the modeling (lines and small symbols).

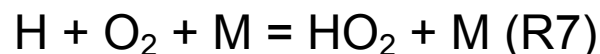


The oxidation of hydrogen in a JSR (1 atm,  $\tau=120$  ms, 1% H<sub>2</sub>,  $\phi=2$ , dilution by nitrogen, 10% H<sub>2</sub>O). The data (large symbols) are compared to the modeling (lines and small symbols).

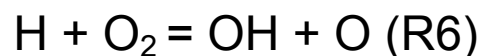
## Hydrogen-H<sub>2</sub>O oxidation: Discussion

The presence of 10% H<sub>2</sub>O in mole reduces the rate of oxidation of H<sub>2</sub>: Hydrogen starts to react at a temperature ca. 50 K higher in presence of H<sub>2</sub>O at  $\phi=0.5$  and 1 atm.

According to our computations, at low temperature due to the higher chaperon efficiency of water compared to that of nitrogen, the presence of water vapor favors the reaction:



This reaction competes with the main branching reaction:



by converting the reactive H atoms into the less reactive HO<sub>2</sub> radicals.

The amount of O atoms also decreases in presence of water vapor through the decreased importance of  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ .

# Hydrogen-H<sub>2</sub>O oxidation: Discussion

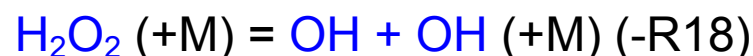
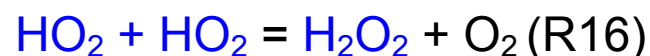
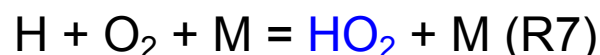
In presence of water vapor in the reacting mixture PSR computations indicated:

(1) an overall **reduced production of OH** via reactions:

**O + H<sub>2</sub> = OH + H (R5)** (10% to **3.4%** at 1000 K and  $\phi = 0.5$ ; 30% to **13%** at 1000K and  $\phi = 2$ )

**H+O<sub>2</sub>=OH+O (R6)** (24% to **17%** at 1000 K and  $\phi = 0.5$ ; 27% to **15%** at 1000 K and  $\phi = 2$ ).

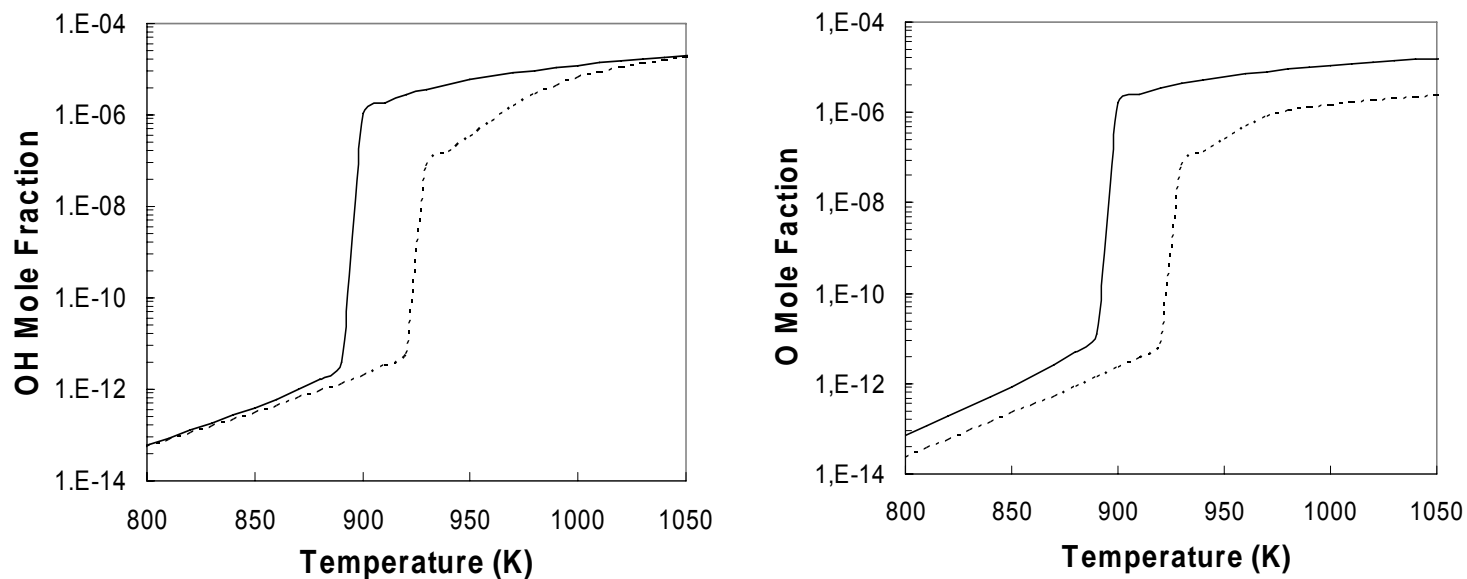
(2) **not compensated** by a too small **increased production of OH radicals** via -R18 through the sequence of reactions:



Also, water reacts with O to yield additional OH at high temperature:



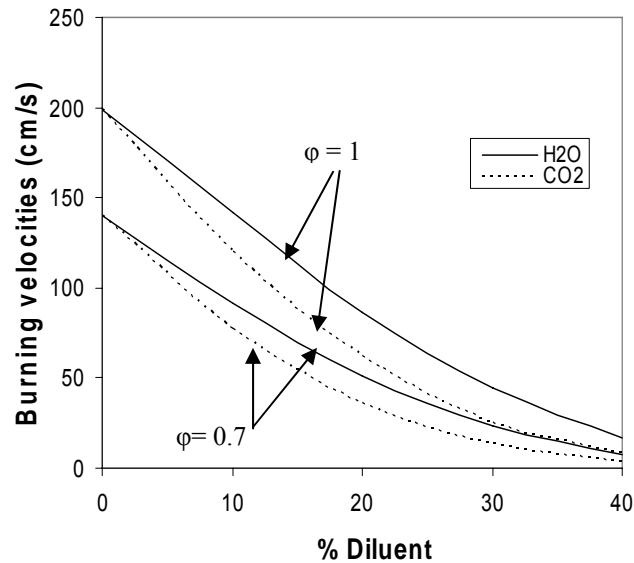
# Hydrogen and Hydrogen-H<sub>2</sub>O oxidation



Computed O and OH profiles during the oxidation of 1% H<sub>2</sub>+O<sub>2</sub>+N<sub>2</sub> w/o (continuous lines) or with 10% H<sub>2</sub>O (dotted lines) at  $\phi=0.5$  and 1 atm.

# Effect of CO<sub>2</sub> and H<sub>2</sub>O on burning velocities

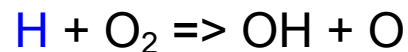
The model predicts a stronger reduction of the burning velocities by dilution with CO<sub>2</sub> than with H<sub>2</sub>O.



Simulated flame speeds of H<sub>2</sub>-air-diluent (CO<sub>2</sub> or H<sub>2</sub>O) at 298K and 1 atm.

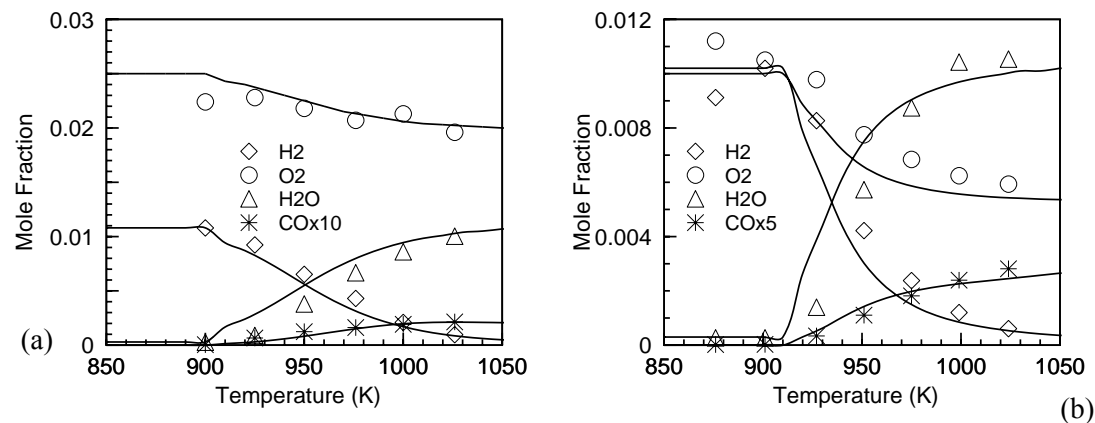
This is essentially due to the **increased importance** of the reaction  $\text{CO}_2 + \text{H} \Rightarrow \text{CO} + \text{OH}$

that reduces the concentration of H and consequently the rate of the main branching reaction

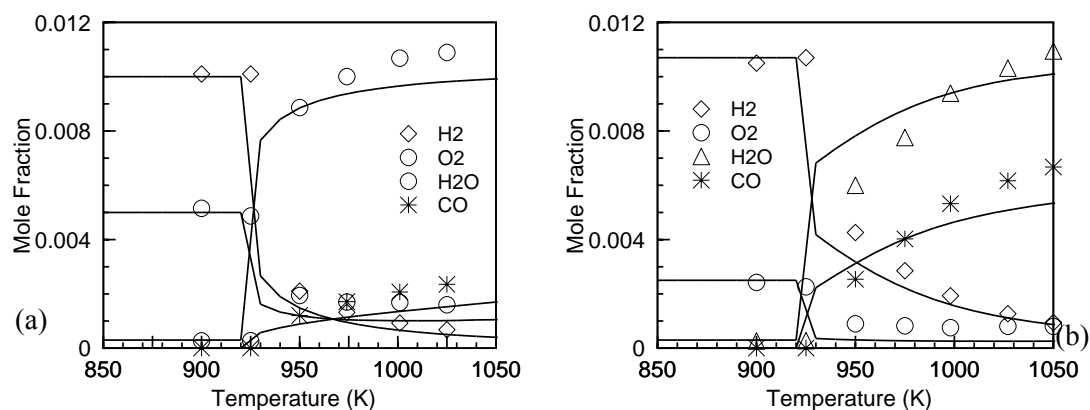


# Hydrogen and Hydrogen-CO<sub>2</sub> oxidation

# Hydrogen-CO<sub>2</sub> oxidation

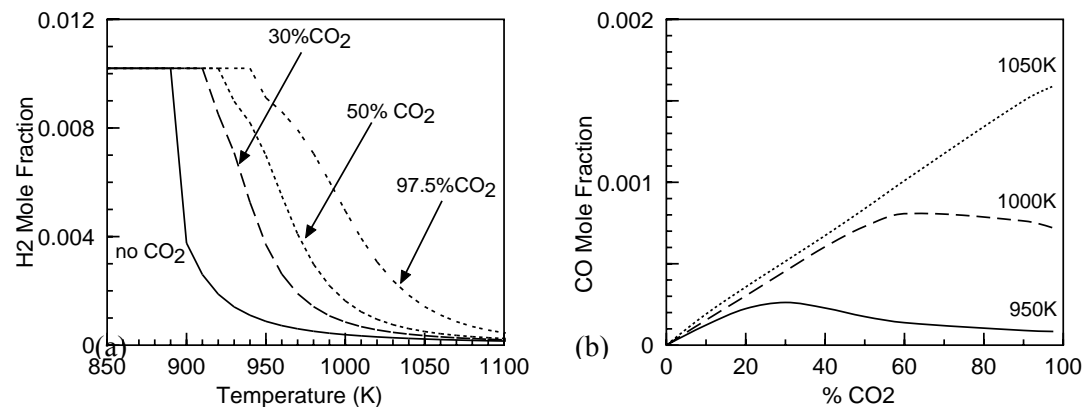


The oxidation of 1% hydrogen and 30% CO<sub>2</sub> in a JSR at 1 atm (a)  $\phi=0.2$ ; (b)  $\phi=0.5$ .

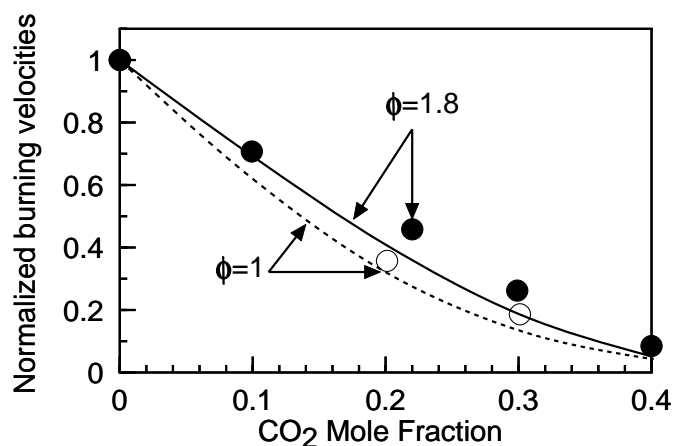


The oxidation of 1% hydrogen and 30% CO<sub>2</sub> in a JSR at 1 atm (a)  $\phi=1$ ; (b)  $\phi=2$ .

# Hydrogen-CO<sub>2</sub> oxidation

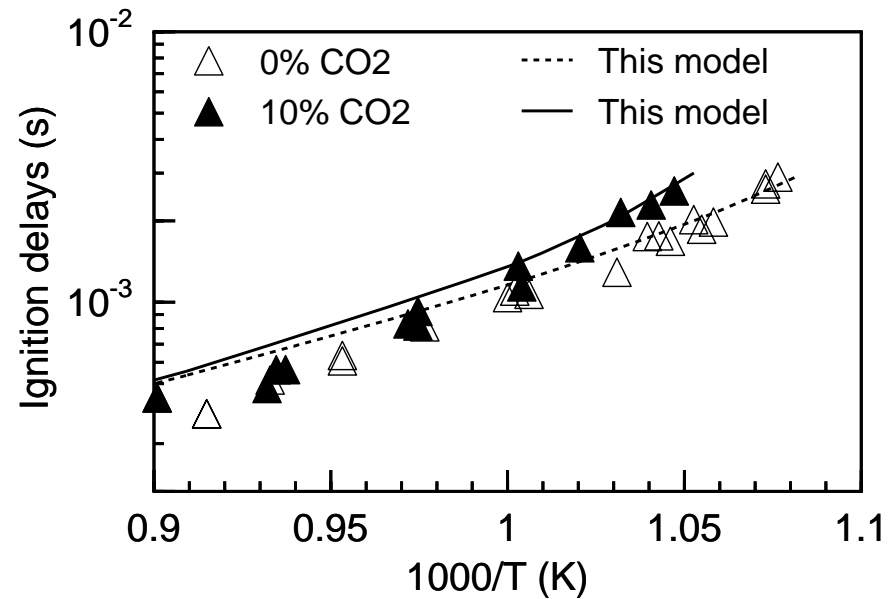


Effect of initial [CO<sub>2</sub>] on JSR hydrogen conversion (a) and CO formation (b). Computations for 1% H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> mixture,  $\phi=0.5$  and 1 atm.



Effect of CO<sub>2</sub> dilution on flame speeds of hydrogen-air mixtures, data from [L. Qiao, C.H. Kim, G.M. Faeth, *Combust. Flame*, 143 (2005) 79].

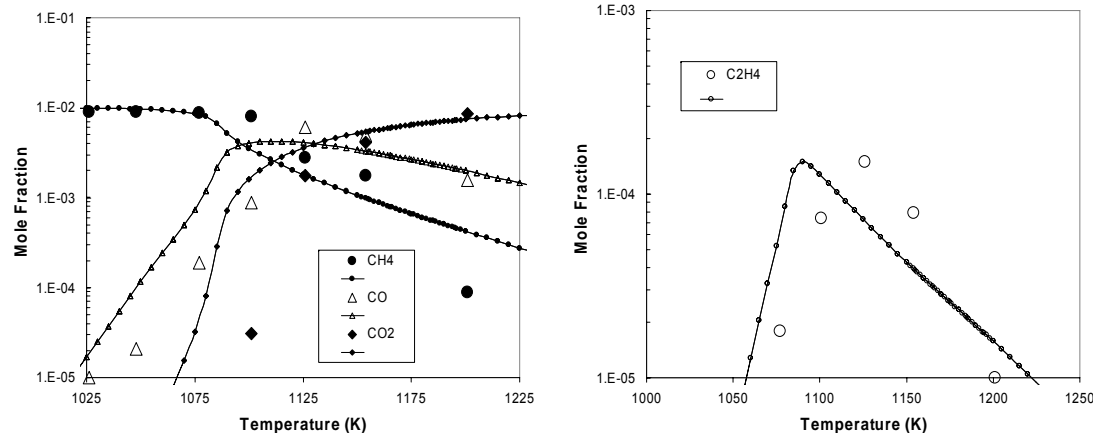
# Hydrogen-CO<sub>2</sub> oxidation



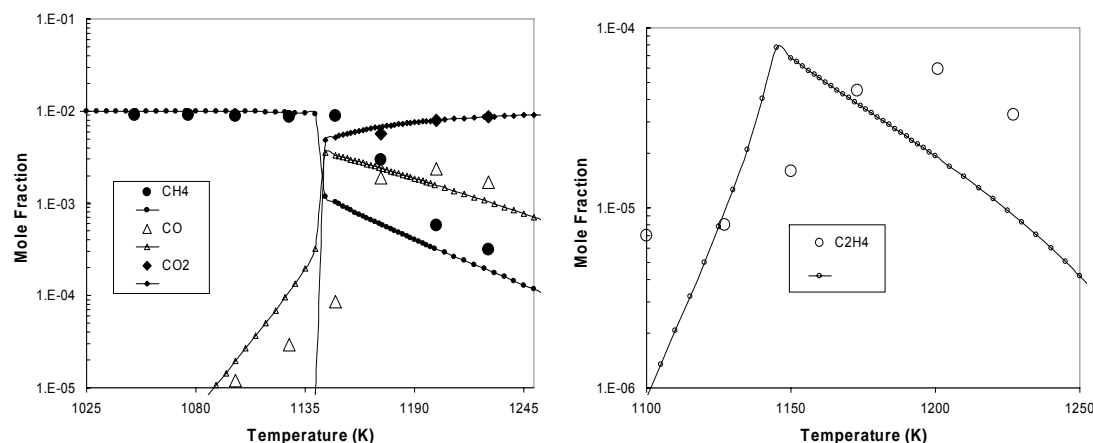
Effect of CO<sub>2</sub> dilution on the ignition of hydrogen, data from [T.A. Brabbs, T.F. Robertson, Report No. TM 100125, NASA, 1987].

# **Methane-and Methane-H<sub>2</sub>O oxidation**

# Methane-H<sub>2</sub>O oxidation



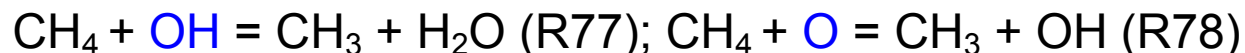
The oxidation of methane in a JSR (1 atm,  $\tau=120$  ms, 1% CH<sub>4</sub>, **10% H<sub>2</sub>O**,  $\phi=0.1$ , dilution by nitrogen). The data (large symbols) are compared to the modeling (lines and small symbols).



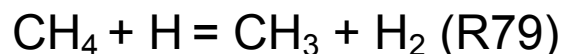
The oxidation of methane in a JSR (1 atm,  $\tau=120$  ms, 1% CH<sub>4</sub>, **10% H<sub>2</sub>O**,  $\phi=0.3$ , dilution by nitrogen). The data (large symbols) are compared to the modeling (lines and small symbols).

# Methane-H<sub>2</sub>O oxidation

In fuel-lean conditions, methane is mostly consumed by reaction with OH and O:



When the equivalence ratio increases, methane reaction with H is increasingly important:



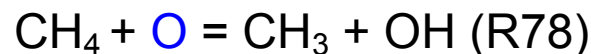
The presence of 10% H<sub>2</sub>O tends to inhibit the oxidation of methane.

Reaction paths analyses for 1%CH<sub>4</sub>-O<sub>2</sub>-N<sub>2</sub> and 1%CH<sub>4</sub>-10%H<sub>2</sub>O-O<sub>2</sub>-N<sub>2</sub> at  $\phi = 0.3$ , 1 atm,  $\tau = 120$  ms, and T = 1140 K: **water participates in the reaction**



This reaction consumes O-atoms (20%) and yields OH (6%).

In absence of water, O-atoms significantly react with methane (80%).



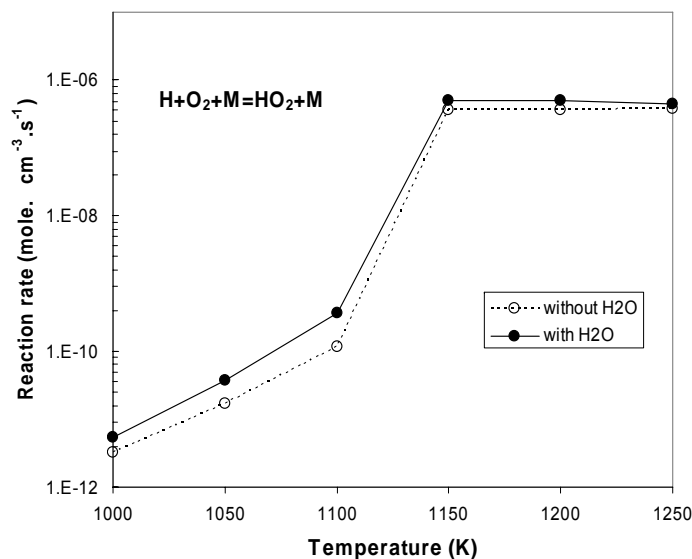
In presence of 10% water, the importance of this channel is reduced to only 60%.

# Methane-H<sub>2</sub>O oxidation

The consumption of H in  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$  (R6) decreases: 45% w/o water down to 38% with water

Its consumption via  $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$  (R7) increases: 10% w/o water to 22% with water

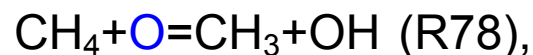
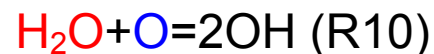
In (R7), the third body efficiency of water, significantly higher than that of nitrogen, is a factor:



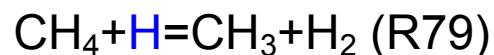
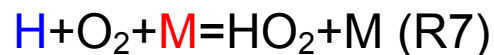
Computed rate for  $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$  during the oxidation of methane and methane-H<sub>2</sub>O in a JSR (1 atm, 1140 K,  $\tau=120$  ms, 1% CH<sub>4</sub>, 0 or 10% H<sub>2</sub>O,  $\phi=0.3$ , dilution by nitrogen).

# Methane-H<sub>2</sub>O oxidation

Furthermore, the competition between the reactions R10 and R78,



and that between the reactions (R7) and (R79)

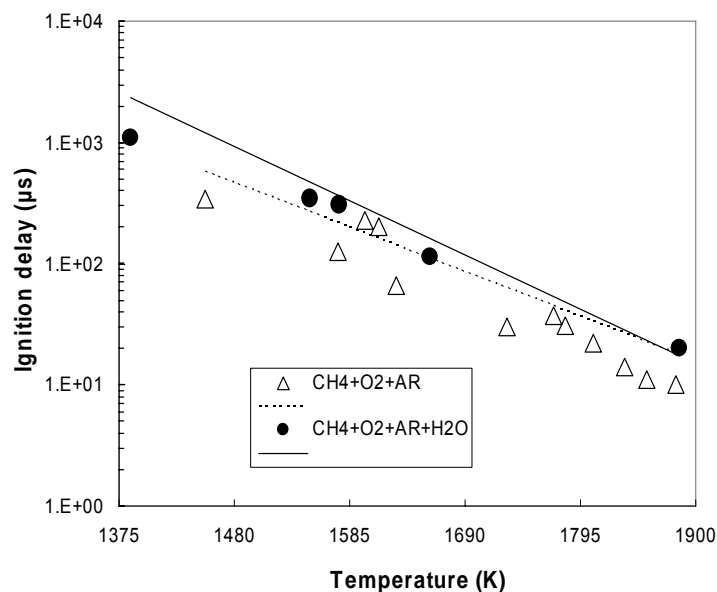


result in a slower consumption of CH<sub>4</sub> in presence of water:

**water inhibits the oxidation of methane under the JSR conditions.**

# Methane-H<sub>2</sub>O ignition

Gurentsov et al. [[High Temperature 40, 379-386, 2002](#)] have measured the ignition delays of mixtures of methane in presence of H<sub>2</sub>O in a shock-tube.



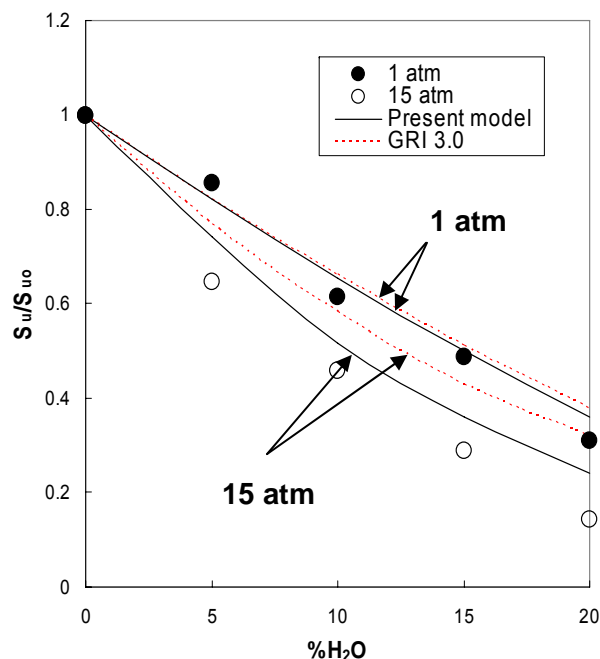
Ignition of methane-O<sub>2</sub>-Ar and methane-O<sub>2</sub>-Ar-H<sub>2</sub>O mixtures; effect of dilution by water vapor. The data (symbols) are compared to the modeling (lines). Mixtures: 9.5%CH<sub>4</sub>-19%O<sub>2</sub>-71.5%Ar and 8% CH<sub>4</sub>-8% H<sub>2</sub>O-17% O<sub>2</sub>-67% Ar ; P = 3.3 – 7.6 atm ; T = 1455 – 1885 K from [Gurentsov et al. \(2002\)](#)

**The present model predicts the increase of ignition delays in presence of water.**

The modeling also indicated a decreased reactivity of the mixture in presence of water results from the same reaction paths delineated under JSR conditions.

# Methane-H<sub>2</sub>O burning velocities

Several studies have demonstrated that water reduces the burning velocity of hydrocarbons.

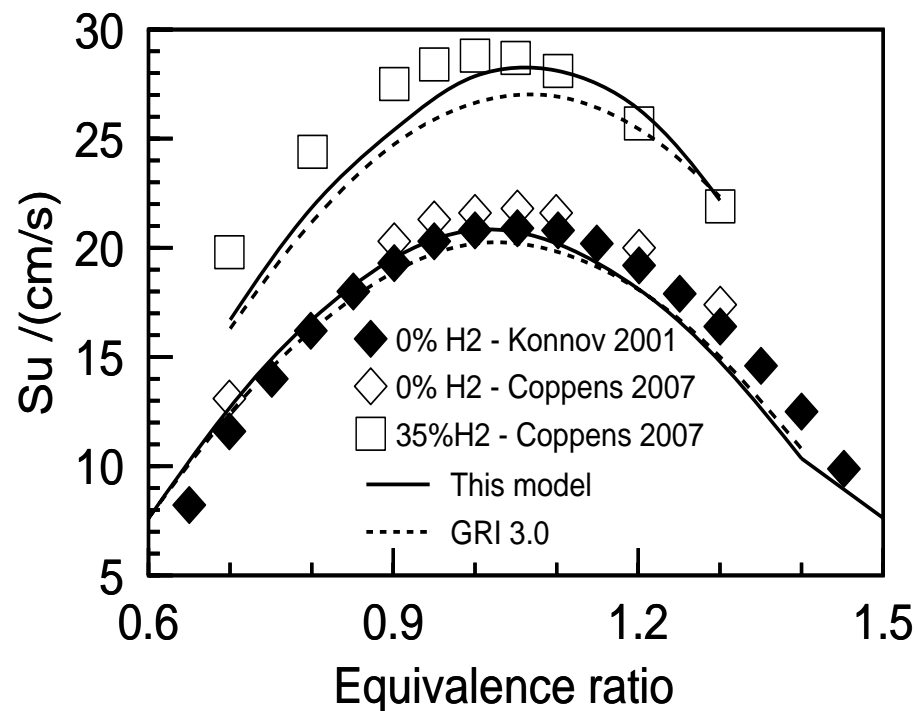


Effect of H<sub>2</sub>O on the burning velocities of stoichiometric CH<sub>4</sub>-air mixtures at 200 °C. The data of Babkin, V'yun (1971) [[Combust. Expl. Shock Waves 7, 339-341](#)] are compared to the modeling (lines).

The present model predicts well the **reduced burning velocities** of methane-air flame at 1 and 15 atm in presence of H<sub>2</sub>O.

# **Methane-hydrogen and Methane-hydrogen-CO<sub>2</sub> oxidation**

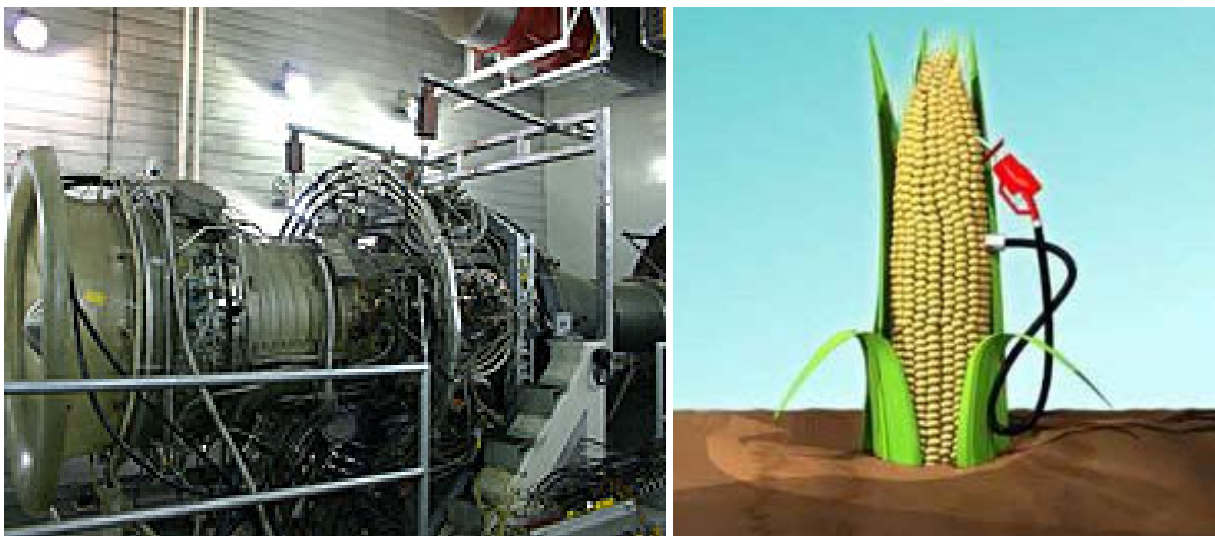
# Methane-CO<sub>2</sub> burning velocities



Effect of initial concentration of hydrogen on flame speeds of methane - CO<sub>2</sub> - air ( $O_2/(O_2+CO_2)=0.3155$ ); data from [A.A. Konnov, I.V. Dyakov, J. De Ruyck, *Proc. 17th Int'l Symposium on Combustion Processes*, Poznan, Poland, September 24 - 27, 2001, pp. 171-177 and F.H.V. Coppens, A.A. Konnov, *21st Int'l Colloquium on the Dynamics of Explosions and Reactive Systems*, 23-27 July, 2007, Poitiers, France, paper ICDERS21\_0006].

## **II. Liquid fuels oxidation**

# Results: Ethanol, E85



## LPP Combustion uses ethanol in gas turbine technology

By Bryan Sims

*Web exclusive posted Feb. 25, 2008, at 12:55 p.m. CST*

During its recent gas turbine combustor testing, Columbia, Md.-based **LPP Combustion LLC determined ethanol to be a viable biofuel within existing gas turbine combustion systems.** Using ASTM D 4806 spec fuel, the company found that emissions of nitrogen oxides, carbon monoxide, sulfur dioxide and particulate matter (soot) were the same as emissions achieved using natural gas in current dry low emission (DLE) gas turbine combustion technology. Additionally, LPP Combustion determined that the combustion of ethanol produced virtually no net carbon dioxide emissions.

# Ethanol, E85

The oxidation of ethanol was studied in a JSR at 1 and 10 atm (eq. ratio 0.3-2; 890-1250K)

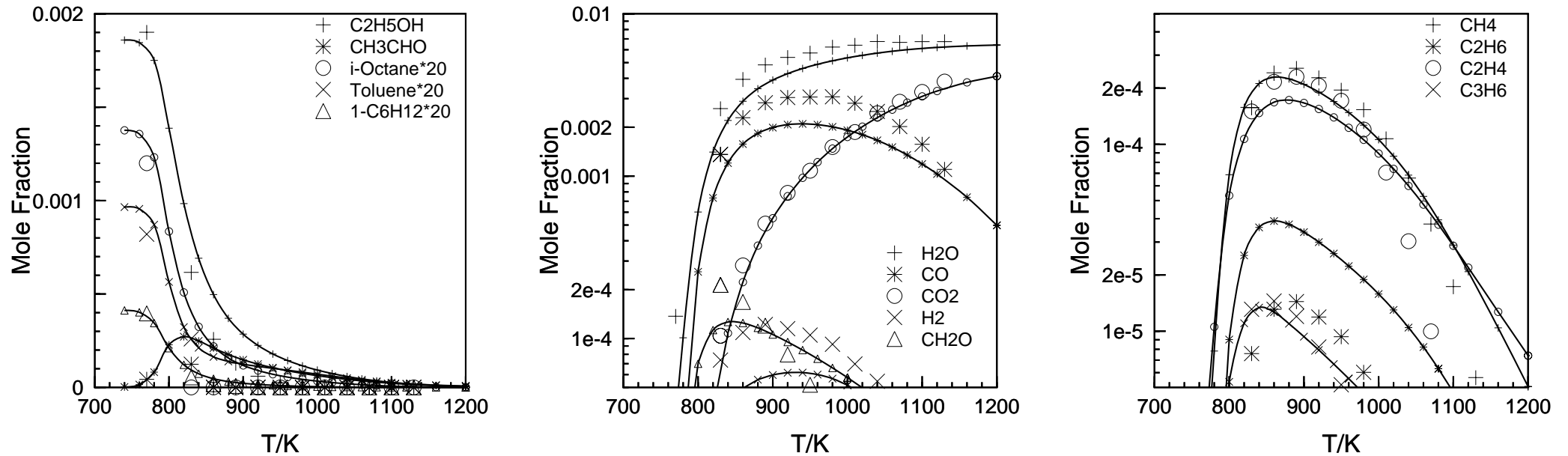
The oxidation of an E85 surrogate fuel was studied in a JSR at 700ms and 10 atm.

*Composition of the reacting mixtures (mole fraction) of the E85 surrogate mixtures:*

<i>Equivalence ratio</i>	<i>Ethanol</i>	<i>Iso-octane</i>	<i>Toluene</i>	<i>1-Hexene</i>	<i>Oxygen</i>
<i>0.3</i>	<i>0.001862</i>	<i>0.000069</i>	<i>0.000048</i>	<i>0.000021</i>	<i>0.02356</i>
<i>0.6</i>	<i>0.001862</i>	<i>0.000069</i>	<i>0.000048</i>	<i>0.000021</i>	<i>0.01178</i>
<i>1</i>	<i>0.001862</i>	<i>0.000069</i>	<i>0.000048</i>	<i>0.000021</i>	<i>0.00707</i>
<i>2</i>	<i>0.001862</i>	<i>0.000069</i>	<i>0.000048</i>	<i>0.000021</i>	<i>0.003534</i>

Kinetic models proposed/validated

# E85



The oxidation of a E85 surrogate fuel mixture in a JSR at 10 atm and  $\phi=0.3$ . Comparison between experimental results (symbols) and modeling (lines and small symbols).

Dagaut and Togbé, *Energy and Fuels* **22** (5), 3499–3505 (2008)

## E85

Simulations performed for the oxidation of the E85 surrogate and the gasoline surrogate, keeping all other parameters constant (residence time, pressure, equivalence ratio, and initial carbon concentration) indicated increased of intermediate concentrations:

acetaldehyde (by a factor of >100)

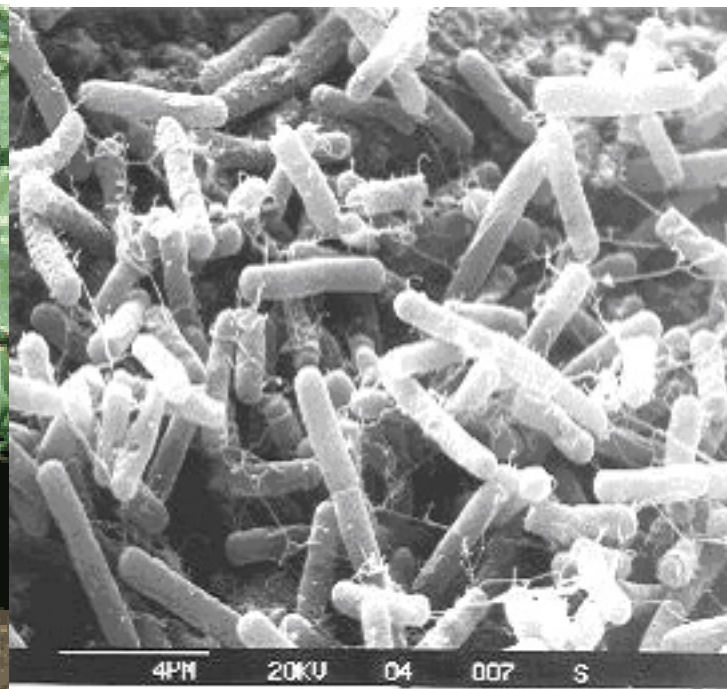
formaldehyde (by ca. 25%),

These findings are in line with light-duty vehicles emissions data [[Yanowitz, J. McCormick, R. L., \*J. Air Waste Manage. Assoc.\* \*\*2009\*\*, 59\(2\)](#)].

# Results: Butanol, Bu85



**Sugar beet**



**Clostridium acetobutylicum, the "Weizmann Organism"**

## Butanol, Bu85

The oxidation of a Butanol oxidation was studied in a JSR at a fixed residence time, at 1 and at 10 atm (eq. ratio 0.25-2; 890-1250K).

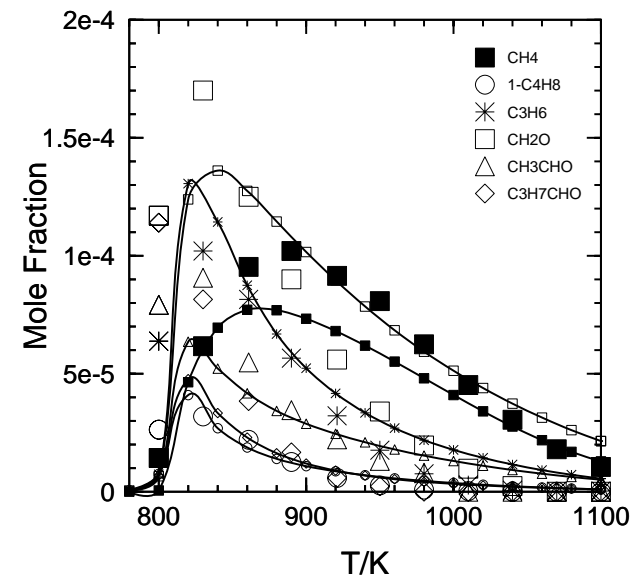
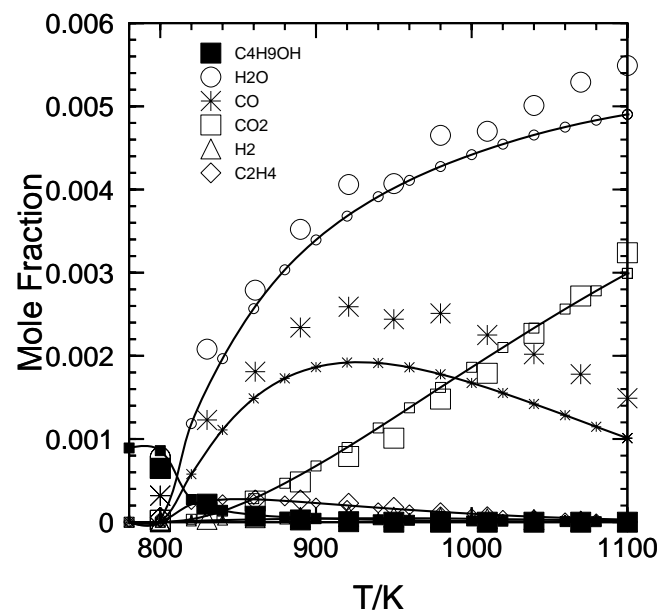
The oxidation of a Bu85 surrogate fuel was studied in a JSR at a fixed residence time of 0.7 s and at 10 atm.

*Composition in mole fraction of the Bu85 surrogate mixtures (85% vol. of 1-butanol).*

<i>Equivalence ratio</i>	<i>1-Butanol</i>	<i>Iso-octane</i>	<i>Toluene</i>	<i>1-Hexene</i>	<i>Oxygen</i>
0.3	0.000896	0.000052	0.0000364	0.0000156	0.021648
0.6	0.000896	0.000052	0.0000364	0.0000156	0.010824
1	0.000896	0.000052	0.0000364	0.0000156	0.006494
2	0.000896	0.000052	0.0000364	0.0000156	0.003247

[Dagaut and Togbé, *Fuel* **87** (15-16) 3313-3321, 2008; Dagaut et al., *Proc. Combust. Inst.* **32**, 229–237, 2009; Sarathy et al., *Combust. Flame* in press 2009]

# Butanol, Bu85



The oxidation of a BU85 surrogate fuel mixture in a JSR at 10 atm and  $\phi=0.3$ . Comparison between experimental results (symbols) with modeling (lines and small symbols)

[Dagaut and Togbé, *Fuel* **87** (15-16) 3313-3321, 2008]

# Results: FAME, RME



# FAME, RME

**ASME Turbo Expo 2008: Power for Land, Sea and Air, Mai 14-17, 2007, Montreal:**

**GT2007-27212: Gas Turbines in Alternative Fuel Applications: Biodiesel Field Test**

**M. Molière, E. Panarotto, M. Aboujaib, J.M. Bisseaud, A. Campbell, J. Citenno, P.-A. Maire, and L. Ducrest**

**GT2007-27652: Impact of Biodiesel on Fuel Preparation and Emissions for a Liquid Fired Gas Turbine Engine**

**C. Bolszo, V. McDonell, S. Samuelsen**

**ASME Turbo Expo 2008: Power for Land, Sea and Air, June 9 – 13, 2008, Berlin:**

**GT2007-28326: Combustion Performance of Liquid Bio-Fuels in a Swirl-Stabilized Burner**

**D. Sequera, A.K. Agrawal, S.K. Spear, D.T. Daly**

**GT2007-27652: Impact of Biodiesel on Fuel Preparation and Emissions for a Liquid Fired Gas Turbine Engine**

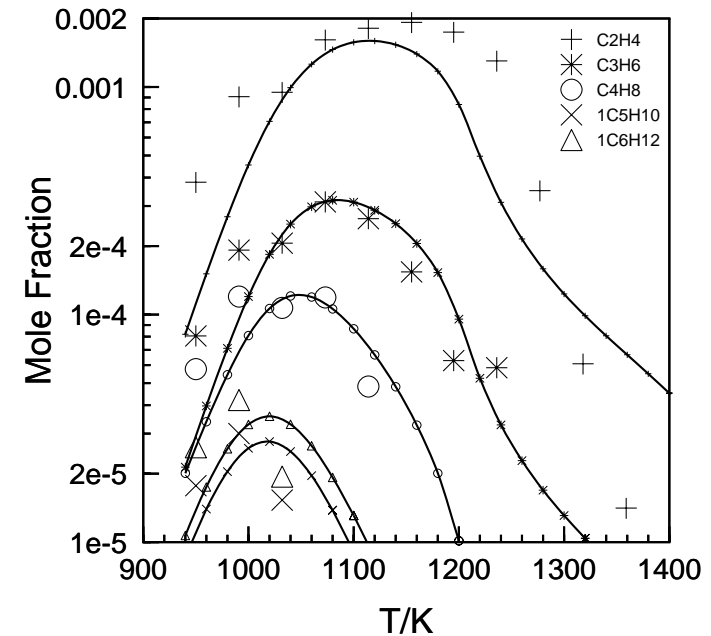
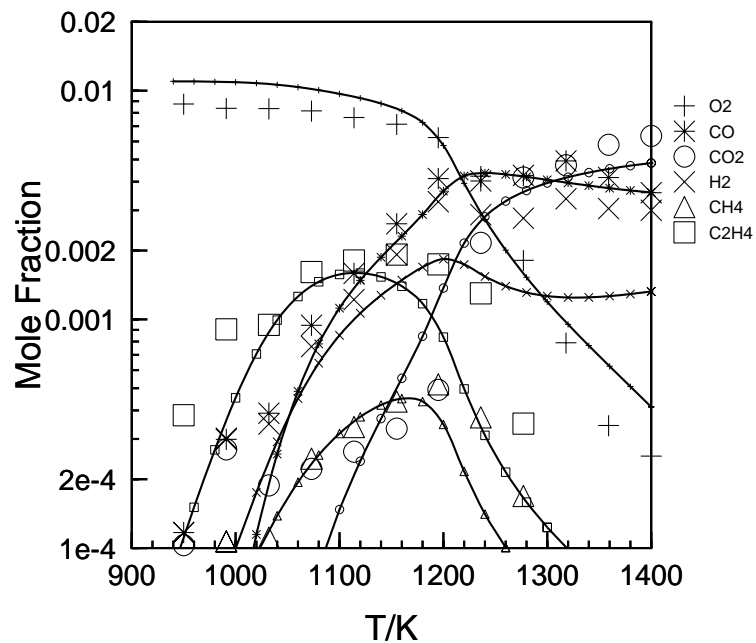
**C. Bolszo, V. McDonell, S. Samuelsen**

**GT2008-51368: Heavy Duty Gas Turbine Fuel Flexibility**

**A. Campbell, T. Healy, M. Moliere, R. Washam, J. Goldmeer, J. Citenno**

# FAME, RME

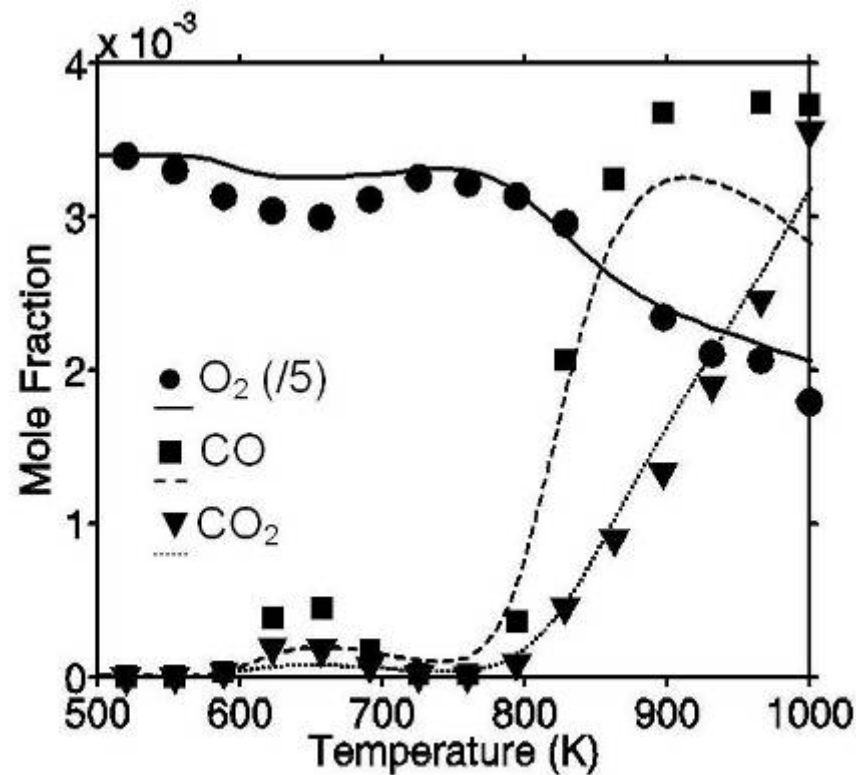
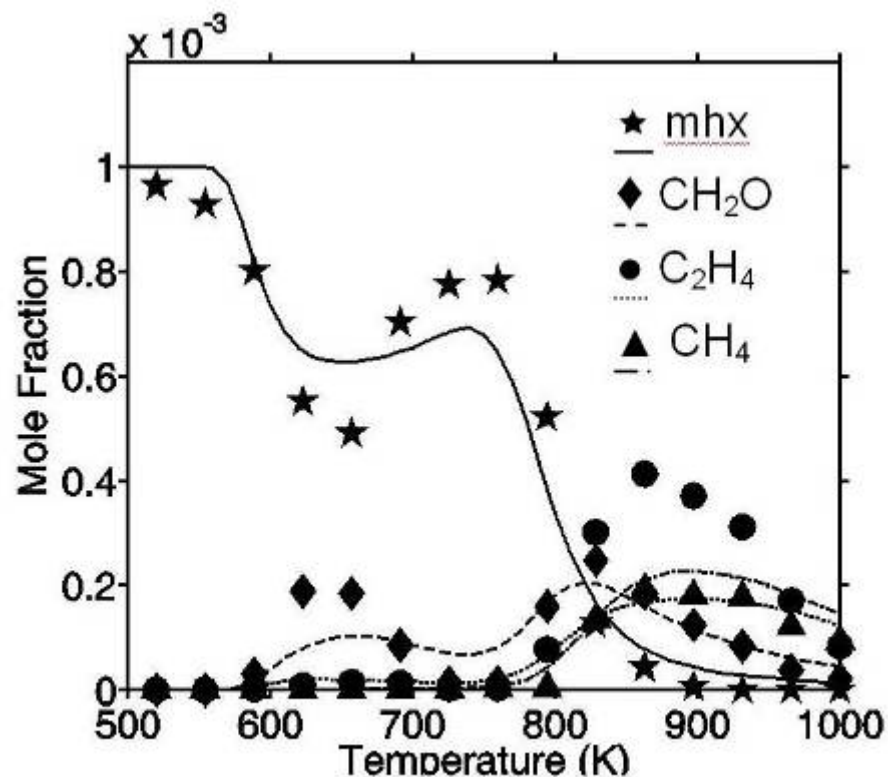
The oxidation of a RME and Methyl-esters (methyl acetate to methyl decanoate) was studied in a JSR at a fixed residence time, at 1 - 10 atm (eq. ratio 0.25-2; 550-1250K).



The oxidation of RME in a JSR at 1 atm ( $\phi = 1$ , 0.07 s). The data (large symbols) are compared to the computations (lines, small symbols), n-hexadecane as surrogate model-fuel.

P. Dagaut, S. Gail, M. Sahasrabudhe, *Proc. Combust. Inst.*, **31**, 2955-2961 (2007)

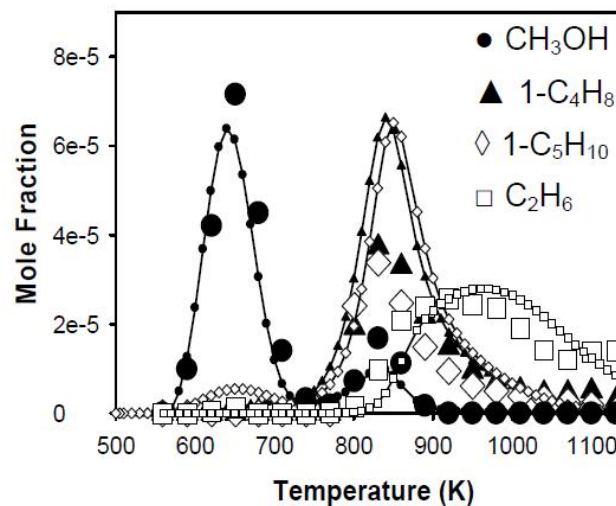
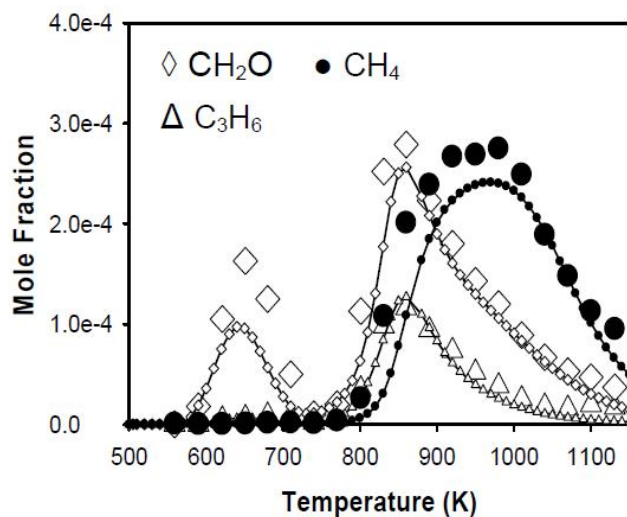
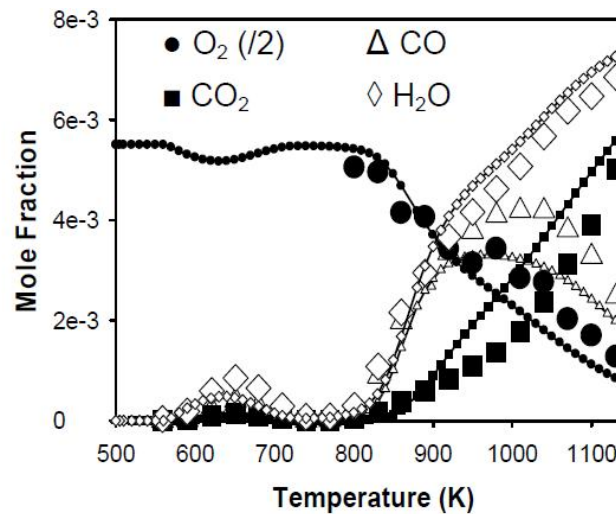
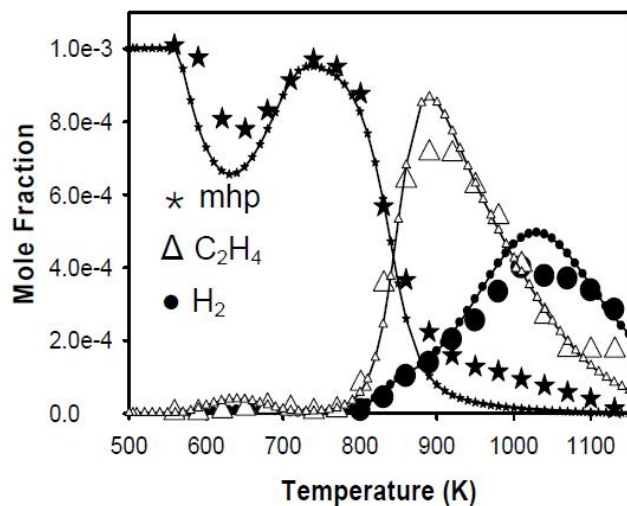
# FAME, RME



Methyl hexanoate oxidation in a JSR at 10 atm,  $t = 1$  s and eq. ratio = 0.5. Experimental data (symbols) are compared to calculations (lines).

[Dayma et al. \*Energy and Fuels\* 22 \(3\), 1469-1479 \(2008\)](#)

# FAME, RME



Methyl heptanoate oxidation in a JSR at 10 atm,  $t = 1$  s and eq. ratio = 1.

[Dayma et al. Energy and Fuels, submitted \(2009\)](#)

## Concluding remarks

The kinetic modeling indicates the effect of water vapor addition under JSR conditions mainly results from the high third body efficiency of H<sub>2</sub>O to remove H in  $H + O_2 + M = HO_2 + M$  and by the reaction of H<sub>2</sub>O with O.

The effect of CO<sub>2</sub> addition under JSR conditions mainly results from the competition between the reaction  $CO_2 + H = CO + OH$  and reactions producing important radicals,

The production of H and OH in presence of hydrogen in methane mixtures is mainly due to reactions in the H<sub>2</sub>-O<sub>2</sub> system,

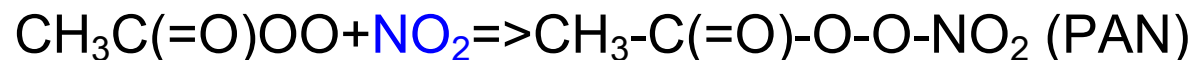
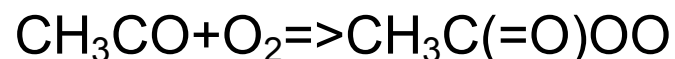
When hydrogen is added to methane at high pressure, H radicals are also produced by the reaction  $CH_3 + H_2 = CH_4 + H$ , and the formation of OH radicals is favored by the decomposition of H<sub>2</sub>O<sub>2</sub>. In flames, the increased concentration of H<sub>2</sub> yields higher flame speeds and the dilution by CO<sub>2</sub> yields lower burning velocities of fuel mixtures.

In premixed flames, the increased concentration of H<sub>2</sub>O yields lower flame speeds, lower adiabatic temperature (reduced NO<sub>x</sub> formation).

## Concluding remarks

Ethanol produces large amounts of **acetaldehyde** during its oxidation

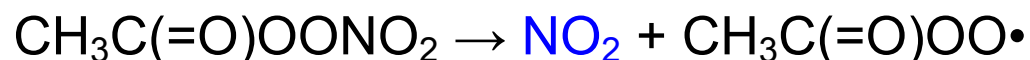
Atmospheric studies indicated [PAN] and O<sub>3</sub> increase



PAN acts as odd nitrogen reservoir (NO and NO<sub>2</sub>); it can be transported away from production region

## Concluding remarks

When PAN decomposes, it reforms nitrogen dioxide:



Photolysis of  $\text{NO}_2$  produces ozone in the troposphere:



O-atom reacts with  $\text{O}_2$  and another body (M) within the troposphere to form ozone:



**Butanol** seems less harmful (less volatile, no increase of acetaldehyde)

## Concluding remarks

FAME kinetics of oxidation is similar to that of corresponding n-alkanes (RME vs. n-hexadecane)

To predict unburnt chemicals: **need to consider the ester function**

Methyl heptanoate or octanoate (ca. 4500 rxns): probably appropriate simple **surrogate** fuel for FAME; Methyl decanoate too large.

# Acknowledgments

Financial support from the Energie research program of CNRS

Drs. G. Dayma, T. Le Cong, and A. Nicolle  
C. Togbé, A. Mze Ahmed

The Organizers of the British-French Flame Days 2009

