

## Combustion Research at University of Groningen

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In this presentation I will give a short summary of current research activities in the area of combustion at the Energy Conversion Laboratory of the Energy and Sustainability Research Institute Groningen.

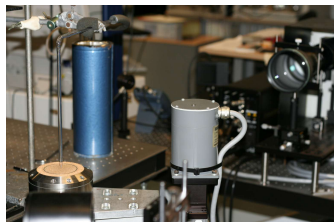
- 1 Research specialization.
- 2 Experimental facilities.
- 3 Diagnostical methods.
- 4 Recent results.
- 5 Undergoing studies.
- 6 Future plans.

Our research activities are aimed at obtaining fundamental insight into the behavior of high temperature reacting systems such as flames and low temperature plasma's. Toward this aim,

- We develop and use a broad spectrum of optical-diagnostic methods.
- Based on the insight gained through fundamental combustion research we provide engineering models and guidelines to manufacturers of energy conversion equipment.

The combustion research at UG has grown from the collaboration between the University of Groningen and the N.V. Nederlandse Gasunie resulting in creating in 1998 the Chair of Combustion Engineering. Currently, combustion research is carried out in the Chair of Energy Conversion which is a part of the Energy and Sustainability Research Institute Groningen.

In our climate controlled laboratory our current facilities include fully controlled (flow rate and gas mixture) combustion systems



- Atmospheric pressure 1- and 2-D flames (3 benches)

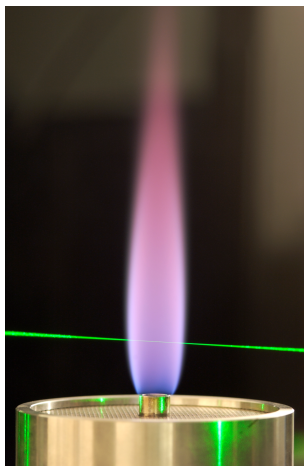


- Low-pressure (low to 20 torr) flames



- Optically accessed Rapid Compression Machine (design pressure 40 Bar).
- Optically accessed combustion chamber for turbulent flames (up to 50 kW, presently mothballed).
- High-temperature atmospheric-pressure ovens (up to 1900 K).

Our diagnostic facilities include an array of lasers, spectrometers, CCD camera's with which we perform the following diagnostics:

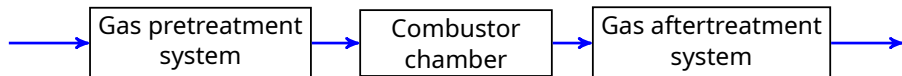


- Spontaneous Raman scattering for thermometry and major species.
- Coherent anti-Stokes Raman scattering for  $N_2$  thermometry.
- Laser-induced fluorescence for trace components (NO, CO, OH, CH).
- Tunable diode laser spectroscopy in the near IR for various species.
- Cavity ring-down spectroscopy from UV (220 nm) to IR ( $3.7 \mu\text{m}$ ).
- Laser-Induced Incandescence (LII) for measuring soot parameters.

Optical methods are complemented by probe measurements.

Ideal Combustion Device is able to

- 1 burn all gases,
- 2 operate at (almost) 100% efficiency,
- 3 produce no pollutants.



At present time this device does not exist! Why? Because complex combustion processes make it's creation extremely difficult (almost impossible). Unfortunately, very often, in discussions about environment issues it is assumed that this device well exists. From other side, it is also (or even more frequently) postulated that creating this device is impossible.

Currently we are in “Energy Transition” phase aimed to get rid of using fossil fuels. According present scenario's, natural gas will be gradually replaced by hydrogen.

Let's make simple calculations.

- $\text{CH}_4 + 2 \text{O}_2 \longrightarrow \text{CO}_2 + 2 \text{H}_2\text{O}(\text{liq}) + 889 \text{ kJ/mol}$
- $\text{H}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O}(\text{liq}) + 286 \text{ kJ/mol}$

Heat release from oxidizing 1 mole of  $\text{CH}_4$  is **3 times larger** than that of  $\text{H}_2$ ! It has interesting consequences for partial replacement of hydrocarbon fuels by hydrogen for decreasing  $\text{CO}_2$  emissions.

Thus burning of  $1 \text{ m}^3$  of methane produces 35.89 MJ of energy. To produce exactly the same amount of energy, we need  $35.89/3.6 \sim 10 \text{ kWh}$  of electrical energy. Considering present prices,  $0.88 \text{ €/m}^3$  for gas and  $0.22 \text{ €/kWh}$  for electricity, burning gas is still 2 times cheaper.



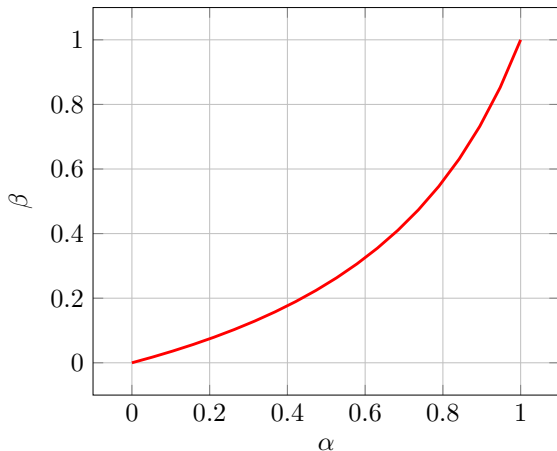
Consider a gas mixture containing  $\alpha$  mole parts of  $H_2$  and  $1 - \alpha$  mole parts of  $CH_4$ . In the “Energy Transition” discussions mainly this parameter  $\alpha$  is used.

However, because the calorific value of mixture is lower than that of  $CH_4$  it should be compensated by burning more gas to provide the same heat output. If this taken into account, then the “real”  $CO_2$  reduction coefficient is

$$\beta = 1 - (1 - \alpha) \frac{\Delta H_{CH_4}}{\Delta H_{mix}} = \frac{\alpha \Delta H_{H_2}}{\alpha \Delta H_{H_2} + (1 - \alpha) \Delta H_{CH_4}},$$

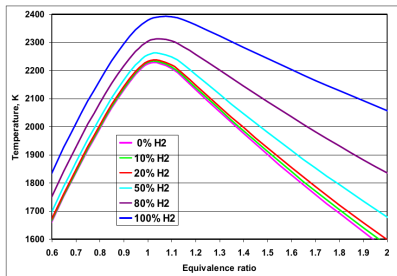
where  $\Delta H_{CH_4}$  and  $\Delta H_{H_2O}$  are heats of combustion of  $CH_4$  and  $H_2$ , respectively.

Reduction of CO<sub>2</sub> emission as a function of H<sub>2</sub> fraction in H<sub>2</sub>/CH<sub>4</sub> mixture



Using 50%H<sub>2</sub>/50%CH<sub>4</sub> mixture results only in 25% reduction of CO<sub>2</sub> emission!

Thus before implementing partial replacement of natural gas by hydrogen, it is a good idea first to check whether other options, for example, improving thermal isolation, are more efficient for CO<sub>2</sub> reduction.



Adiabatic flame temperatures of H<sub>2</sub>/CH<sub>4</sub> blends.

- 200 K difference between temperatures of hydrogen and methane flames.
- Because of high sensitivity of combustion chemistry to temperature, significant differences in combustion properties of H<sub>2</sub> and CH<sub>4</sub> flames are expected.
- Solution can be sought in using hydrogen flames with equivalence ratio's smaller than those of methane flames. Are these flames stable?

As an alternative to hydrogen, other fuels are proposed.

- Ammonia  $\text{NH}_3$ .

Advantages:

- Does not produce  $\text{CO}_2$  and soot.
- High energy density (Liquid at normal conditions).
- Good developed infrastructure and transportation facilities.
- Can be produced from renewable energy.

Disadvantages:

- High corrosive and toxic.
- High tendency of NO formation.
- Very poor combustion properties.

- Dimethyl Ether  $\text{CH}_3\text{OCH}_3$ .

Advantages:

- Low tendency of soot formation.
- Low tendency of NO formation.
- High energy density.
- High cetane number ( $> 55$ ).

Disadvantages:

- Produces  $\text{CO}_2$  in combustion.
- Lower calorific value than that of diesel.

**Solution:** Use blends of fuels such as  $\text{NH}_3/\text{H}_2$  or  $\text{NH}_3/\text{DME}$ .

For effective use of these blends their combustion properties should be known.

Towards these aim we perform studies of ignition delay times, laminar burning velocities and structures of diffusion flames of mixtures of ammonia with various fuels at experimental conditions relevant to practical applications.

- Mixtures of fuel and oxidizer are indefinitely stable at room temperature, but at higher temperatures they “ignite”.
- In combustible mixtures, ignition/propagation only occurs within a range of ratio of fuel/oxidizer.

The reason for this is

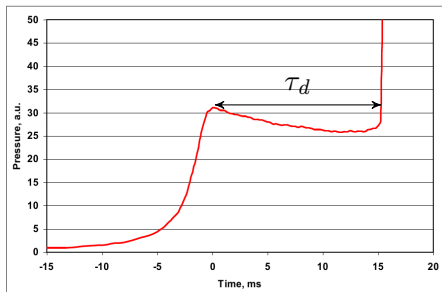
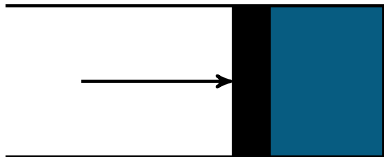
- Probability of collision of more than 2 molecules is very low.
- Reactions have a very large **activation energy**.

Combustion occurs through the very complicated **free radical chain mechanism of oxidation**. The amount of radicals grows with time, and more and more fuel and oxidizer will be converted into products. This exponential growth will result in explosion of the unburned mixture. Time between bringing the unburned mixture to a specific state and moment of explosion is called **ignition delay time**  $\tau_d$ .

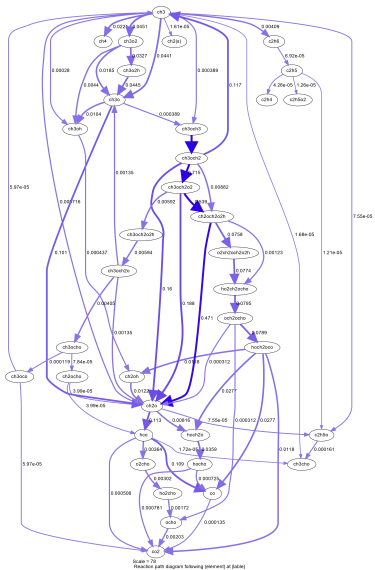
$t = -15 \text{ ms}$



$t = 0 \text{ ms}$

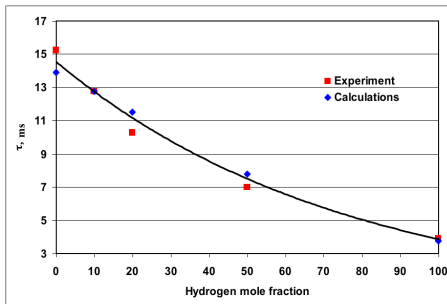


Pressure trace in 10% $\text{H}_2$ /90% $\text{CH}_4$  mixture compressed to pressure 31.3 Bar at temperature 995 K (Gersen et. al. Int. J. Hydrogen Energy, 2008).



- Chemical mechanisms are very complex, usually include more than 100 reactions.
- Rates of chemical reactions are known with very low accuracy (30% at best, usually one order of magnitude).
- Usually obtained by fitting experimental data over ignition delay times and laminar burning velocities.
- As an example, flux of carbon atoms during ignition of Dimethyl Ether (DME) is shown left.



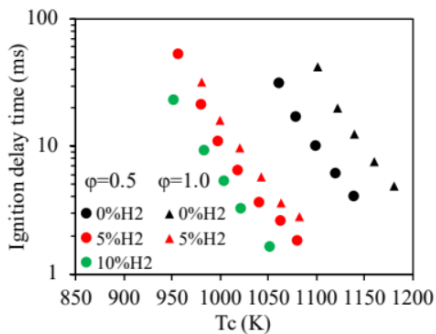


H<sub>2</sub>/CH<sub>4</sub> mixture is compressed to 33.5 bar at temperature 995 K (Gersen et. al. Int. J. Hydrogen Energy, 2008).

- Ignition delay time in H<sub>2</sub> is shorter than that in pure methane.
- For mixtures the following empirical relation is proposed:

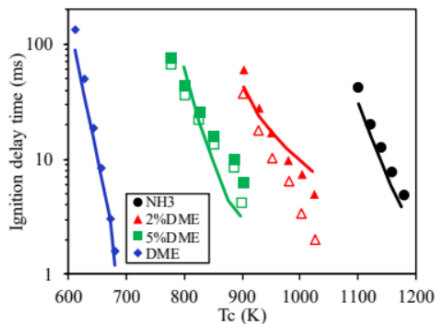
$$\tau = (\tau_{H_2})^\beta (\tau_{CH_4})^{1-\beta}$$

where  $\beta$  is a mole fraction of H<sub>2</sub> in mixture and  $\tau_{H_2}$  and  $\tau_{CH_4}$  are ignition delay times in pure H<sub>2</sub> and CH<sub>4</sub>, respectively.



$\text{NH}_3/\text{H}_2$  mixture is compressed to 60 bar (Dai et. al. Combust. Flame, 2020).

- Strong temperature dependence of ignition delay time upon temperature.
- $\text{NH}_3$  ignites at high ( $> 1100$  K) temperatures
- Ignition delay times are larger at  $\phi = 1.0$  than those at  $\phi = 0.5$ .
- Significant ignition-enhancing effect of  $\text{H}_2$ . Ignition delay time decreases  $\sim 10$  times when 5%  $\text{H}_2$  is added to  $\text{NH}_3$ .



NH<sub>3</sub>/DME mixture is compressed to 60 bar (Dai et. al. Combust. Flame, 2021).

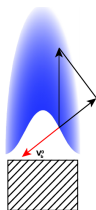
- Similar to NH<sub>3</sub>/H<sub>2</sub> mixtures strong temperature dependence of ignition delay time upon temperature.
- Addition of 5% DME to NH<sub>3</sub> results in decreasing ignition temperature by  $\sim 300$  K.
- Ignition-enhancing effect of DME is even more pronounced than that of H<sub>2</sub>.

By definition, burning velocity  $v_b$  is propagating speed of 1-D flame front relatively to unburned fuel/oxidizer mixture. Burning velocity is closely related to stability of premixed flames. Burning velocity depends upon composition, equivalence ratio and temperature of unburned fuel/oxidizer mixture.

$$v_b = v_f$$



$$v_b < v_f$$

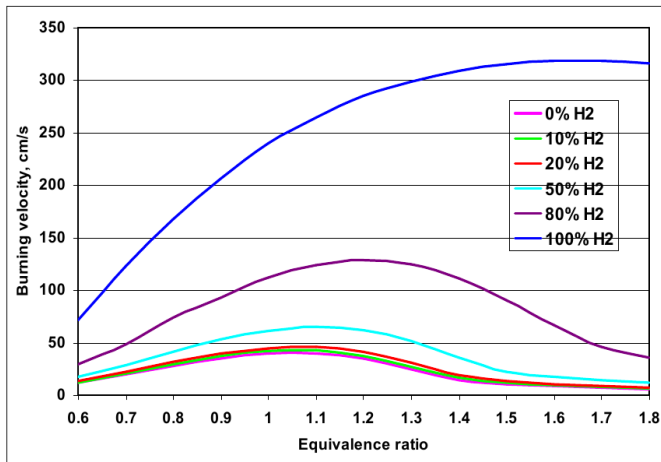


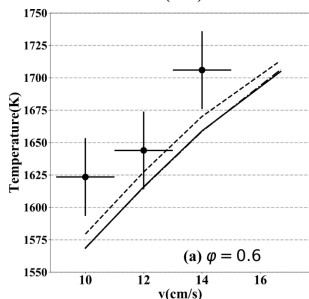
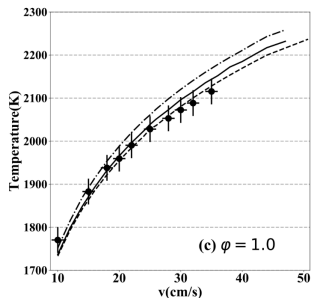
$$v_b > v_f$$



- Flame is stabilized above a burner when burning velocity equals velocity of unburned gas/air mixture,  $v_b = v_f$ .
- When  $v_b < v_f$  **blow-off** can occur.
- When  $v_b > v_f$  **flash-back** can occur.

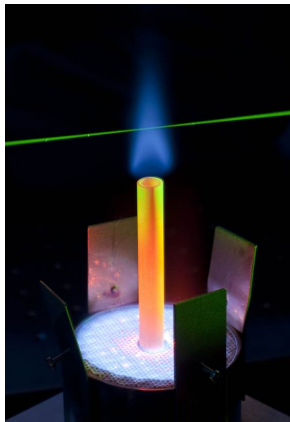
Burning velocity of laminar atmospheric pressure  $H_2/CH_4$  flames as a function of equivalence ratio



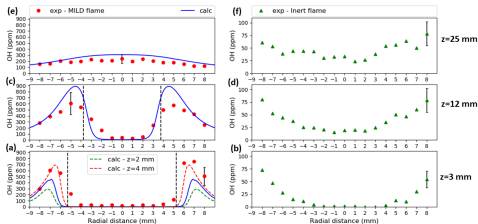
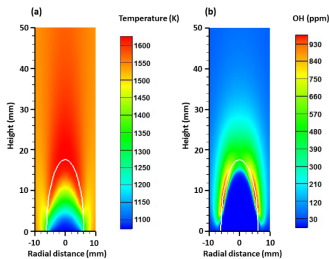


- Burning velocities are determined by measuring temperature of burner stabilized flat flames.
- The burning velocities of DME are close to those of methane.
- Good agreement between calculated and measured temperatures at  $\phi = 1.0$ .
- The chemical mechanisms underpredict the measured flame temperatures at  $\phi = 0.6$ .

Testing “chemistry-flow” interactions are needed because of complexity of combustion process. Towards this aim we are doing studies of structure of axi-symmetric diffusion flames.



- Laminar regime provides good insight into the chemical structure of the flame.
- Simple geometry - relative easy to perform numerical simulations.
- Gradients of temperature and concentrations at atmospheric pressure are relative small to be resolved in standard optical measurements.

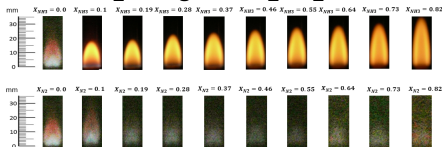


(Nourani et.al. Energy Fuels, 2021)

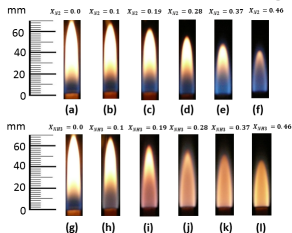
- These studies have been done in collaboration with TUE.
- OH mole fractions are obtained from LIF measurements.
- OH profiles clearly indicate combustion activity.
- Calculations overpredict measured OH mole fractions.



## $H_2/NH_3$ vs. $H_2/N_2$

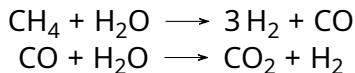


## $CH_4/N_2$ vs. $CH_4/NH_3$

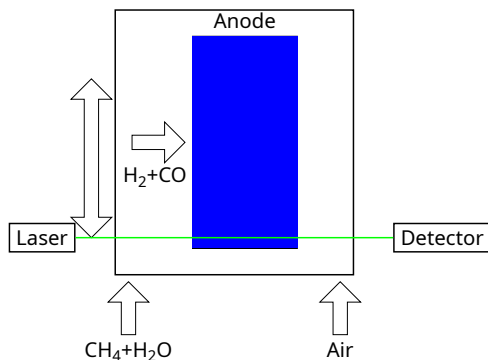


- Flames ceased to exist at  $NH_3$  fraction larger than 82%.
- $N_2$  is used as a fuel additive to distinguish chemical effects of  $NH_3$  addition.
- Intensive radiation from  $NH_3$  flames due to chemiluminescence processes.
- Chemiluminescence can be used for controlling combustion devices and potentially for direct conversion of chemical energy into light.
- Soot production in  $NH_3/CH_4$  flames is suppressed.

Methane can potentially be used in Solid Oxide Fuel Cells as fuel instead of pure H<sub>2</sub> which can be produced inside SOFC

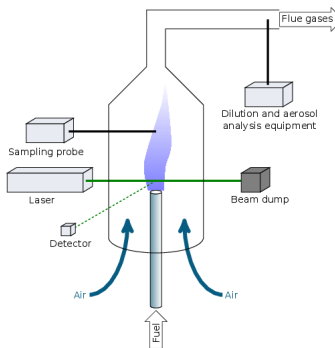


- Internal reforming makes SOFC's more efficient and cost-effective (no heat for an external reformer and less cooling demand for a fuel cell).
- Multiple studies of internal CH<sub>4</sub> reforming in SOFC's based on input/output measuring species fractions are contradicting.
- We propose to measure concentrations of relevant components using laser-based diagnostic techniques.
- CH<sub>4</sub>, H<sub>2</sub>O, CO<sub>2</sub> and CO have intensive lines in IR spectral region and can be measured by Absorption Spectroscopy. H<sub>2</sub> has no absorption spectra in IR, and Spontaneous Raman Scattering is required.



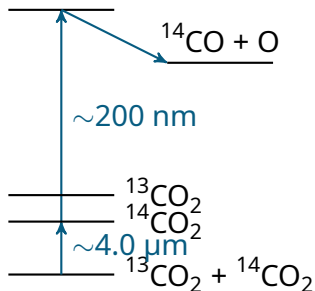
- Tunable Diode Laser Absorption Spectroscopy will be used for measuring  $\text{CH}_4$  concentrations.
- Vertical profiles are measured by moving setup relative to a laser beam.
- Building optically accessed SOFC is underway now.

- Calculations of soot emissions from large-scale turbulent flames such as gas flares are unreliable.
- Multiple reaction paths and differential diffusion result in so-called “synergistic” effect when soot production is higher than that calculated from emissions in pure flames.
- Experimental studies of soot formation at relevant conditions are needed for testing models of soot formation and providing reliable data for evaluation of impact of soot from flares on global climate change.



- Studies of soot formation and reburning will be performed in coflow diffusion flames at conditions close to those in real flares by using LII method.
- To provide more insight into “synergistic” effect, isotopic labeling of a fuel component followed by isotopic analysis of soot particles in exhaust gases will be performed.
- Optical properties of soot particles will be determined.

- Natural abundance of  $^{14}\text{C}$  is  $1 \times 10^{-12}$ , while many practical applications require measuring  $^{14}\text{C}$  below this limit.
- Expensive state-of-the-art systems can reach  $1 \times 10^{-15}$  detection limit.
- Enrichment of a  $^{14}\text{C}$  sample by factor  $\sim 100$  in the **photo-ionization** process with subsequent detecting  $^{14}\text{C}$  containing molecules using a relative simple setup is proposed.
- $^{14}\text{CO}_2$  molecules are first selectively photodissociated. Produced  $^{14}\text{CO}$  and other CO molecules containing various C isotopes are separated from  $\text{CO}_2$  and process is repeated to reach required concentration of  $^{14}\text{C}$ .



- Selective ionization of  $^{14}\text{CO}_2$  is achieved by using a two-step process.
- In a first step a narrow-band pumping laser is used to excite transition in  $^{14}\text{CO}_2$  while rejecting exciting similar transitions in  $^{13}\text{CO}_2$  and  $^{12}\text{CO}_2$ .
- Further increasing selectivity may be also achieved in the second step when transferring  $^{14}\text{CO}_2$  molecules from excited to predissociation states.

- Short description of research activities in the area of combustion research at the University of Groningen is presented.
- Currently, we are active in carrying out studies of ignition phenomena using a Rapid Compression Machine and structures of laminar diffusion flames using Spontaneous Raman Scattering and Laser-Induced Fluorescence techniques.
- In future, we are going to perform the following actions:
  - Critically review the present research activities and abandon non-perspective “bike shedding” studies.
  - As a short term solution, study combustion technologies related to the “Energy transition”.
  - Use developed expertise to collaborate in the inter-disciplinary research areas.



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