Experimental Study on Pollutant Formation in low-pressure Flames of Furanic Biofuels

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Motivation

Biofuels are seen as an interesting and promising alternative to fossil fuels.

Woody biomass → Plant cell walls → Cellulose structure or microfibril → Lignin penetrates → Ionic liquids → Future high-energy fuels DMF/HMF

**Furan family**

- Tetrahydrofuran (THF)
- Furan (F)
- 2-Methylfuran (MF)
- 2,5-Dimethylfuran (DMF)

- From *ligno-cellulosic biomass*
- **Oxygenated fuels** comparable to commercial fuels
- What is their impact on the formation of pollutant emissions?
“Furan family” in literature...

- **Oxidation in laboratory condition:**
  - **Shock Tube** *(Ignition delay time)*
    - ...
  - **Premixed Laminar Flame** *(Kinetics at High T)*
    - ...
  - **Isothermal quartz flow reactor** *(Kinetics at High T)*
    - ...

- **Oxidation in real condition:**
  - **Rapid Compression Machine** *(Kinetics at Low T - Ignition delay time)*
    - FENARD, Y. et al., Combust. Flame, 178 (2017) MTHF
    - ...

- **Nitrogen Oxides:**
Nitrogen Oxides

NO is one of the regulated pollutants formed during combustion. It is produced according to different, more or less well-known, pathways:

**Thermal - NO**

**Prompt - NO**

**Fuel - NO**

It involves intermediate hydrocarbon fragments, particularly CH, reacting with N₂ under fuel rich conditions.

(Lamoureux et al., *Combustion and Flame* 157.10 (2010): 1929-1941.)
Fuel Oxidation

Methane oxidation

\[ CH_4 \xrightarrow{+H, +H,O,OH} \]

\[ \rightarrow CH_3 \]

\[ \rightarrow CH_2 \xrightarrow{+H} CH \]

\[ \xrightarrow{NO} \]

Biofuel Oxidation

\[ H_3C-\overset{\text{O}}{\underset{\text{O}}{\text{O}}} - CH_3 \]

\[ O \]

\[ 5 \]
Objectives

Considere fuels:

- Furan
- Tetrahydrofuran (THF)

Aims of this study:

- **Experimental characterization** of NO formation during Furan and THF combustion

- **Development of a model** for NO formation during Furan and THF combustion

- Discussion on **NO formation routes**
Laminar Premixed Flame

Low pressure Flame

Flame structure

unburned mixture zone
preheat zone
reaction zone
burned gas zone

Species mole fraction
Temperature

x=HAB

HAB = Height Above the Burner
# Operating conditions

<table>
<thead>
<tr>
<th>Flames</th>
<th>$\phi$</th>
<th>*%CH4</th>
<th>*%F</th>
<th>*%THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1.0</td>
<td>1.0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M1.2</td>
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<td>100</td>
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<tr>
<td>THFM1.0</td>
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<tr>
<td>THFM1.2</td>
<td>1.2</td>
<td>50</td>
<td>0</td>
<td>50</td>
</tr>
</tbody>
</table>

*Fuel composition*

- **Pressure**: 5.3 kPa
- **Total Flow**: 5 sL/min
Experimental set-up

- GC-TCD/FID
- GC-MS
- Gas Network (N₂, O₂, CH₄, C₄H₄O)
- Laser Induced Fluorescence
- Premixed Laminar Flame
- Micro-probe
- Species profiles
- Vacuum pump
- Furan vaporization system
- NO, CH, Temperature
- Experimental set-up
Combustion products and stable intermediates
Gas-Chromatography Results

- 6 flames analyzed by gas chromatography equipped with:
  - MS detector
  - FID detector coupled with methanizer
  - TCD detector

- 63 species have been detected globally:
  - 14 in Methane flames
  - 47 in Furan doped flames
  - 49 in THF doped flames
Different pollutants found in Furan and THF flames:

- **Aldehydes**: Formaldehyde, Acetaldehyde, Acrolein, 2-Butenal, Propanal, Cyclopropane-carboxaldehyde,…

- **PAH Precursors**: Acetylene, Propene, Propyne, Allene, 1,3Butadiene, Cyclopentadiene, Benzene,…
**Species profiles**

**Fuel**

Biofuels flames are stabilized closer to the burner surface with respect to Methane flames.

**Furan** is consumed faster than THF.

**Burning velocity**

\[ P = 101 \text{kPa} \quad T = 298 \text{K} \quad \phi = 1 \]

- \( \text{CH}_4^{a} : S_{u\text{CH}_4} = 36.3 \text{ cm.s}^{-1} \)
- \( \text{THF}^{b} : S_{u\text{THF}} = 41.4 \text{ cm.s}^{-1} \)
- \( \text{Furan}^{c} : S_{u\text{Furan}} = 62.5 \text{ cm.s}^{-1} \)

\[ S_{u\text{Furan}} > S_{u\text{THF}} \]

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\(^{a}\text{Dirrenberger et al., Energy Fuel, 25 (2011) 3875-3884}\)

\(^{b}\text{Tran et al., Combustion and Flame, 162 (2015), 1899-1918}\)

Species profiles

**Acetylene formation** is enhanced in furan oxidation

Liu et al., Combust. Flame, 61, (2014) 748-7651

**Ethylene formation** is enhanced in THF oxidation

Tran et al., Combustion and Flame, 162 (2015), 1899-1918
NO measurements
Laser Setup

A-X (0-0) ≈ 226 nm

A-X (0-2) ≈ 247 nm

L1, L2: lens with focal distance 300 mm and 200 mm

6-cm-diameter bronze porous plate water-cooled McKenna burner

Nd-YAG/tunable dye laser (YG-TDL Quantel)

A-X (0-0) ≈ 226 nm

A-X (0-2) ≈ 247 nm

Photodiode

Oscilloscope

PM tube

Spectrometer

PC
Excitation-Detection scheme

Experimental NO LIF excitation spectra.

NO molecules are excited by using the $Q_2(27)$ transition of the $A-X(0,0)$ at 225.58 nm.
NO LIF signal profile

- NO LIF relative profile

\[ \Phi(t) = \frac{GV\Omega}{4\pi} N_{tot} f_b(J'', \nu'', T) B_{12} U\nu \frac{A_{21}}{A_{21} + Q_{21}} \]

- NO doping calibration method in flame M1.0

\[ \chi_{\text{NO native}} = 10.7 \pm 0.1 \text{ ppm} \]

\[ R^2 = 0.997 \]

Calibration curve obtained in flame M1.0, HAB=19 mm
- NO formation is enhanced in **fuel-rich conditions**

- NO formation is enhanced in **Furan flames**:
  - +27% at $\phi=1$ and +11% at $\phi=1.2$
  (with respect to Methane flames in same operating conditions)
Perspectives....

- Measurement of the NO in THF flames and CH profiles in flames by LIF

- Measurement of the temperature profiles in the flames by NO–LIF thermometry

- Detailed chemical kinetic modeling helps the interpretation of the data

  - BioFuel oxidation mechanism available in literature
  - NO mechanism NOMecha2.0* developed in PC2A laboratory

*Lamoureux et al. Combust. Flame 163, 2016*
Thanks for the attention