Etude Expérimentale et de Modélisation de la Cinétique d'Oxidation des Dérivés du Tétrahydrofurane à Haute Pression

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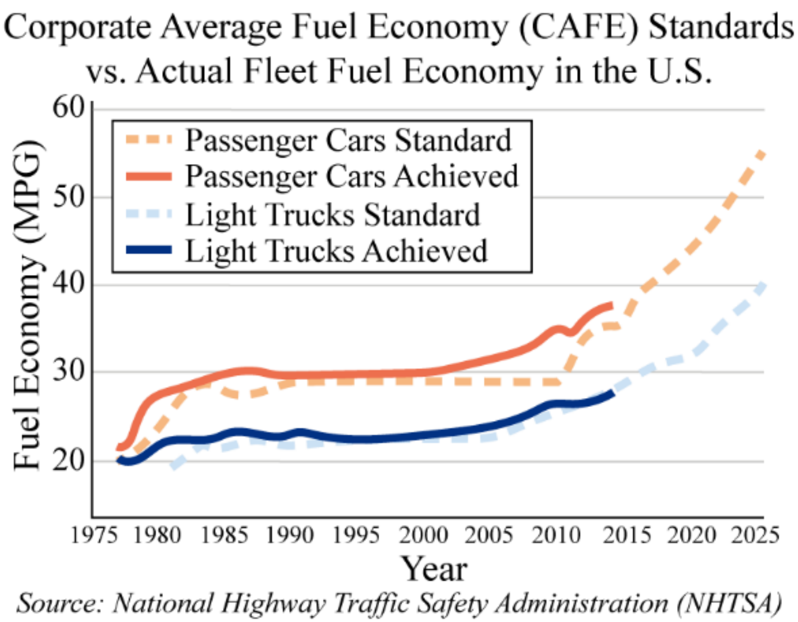
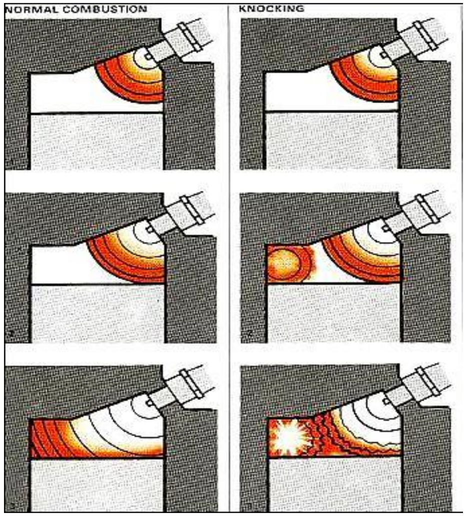
Presentation for *Combustion de Biocarburants, de la Biomasse et de ses Derives*
7.11.2017 – 8.11.2017, Cité Scientifique, Villeneuve d'Ascq

Introduction: Stringent regulations

- Engine runs under severe conditions than before.





Normal and knocking combustion (www.autospeed.com)

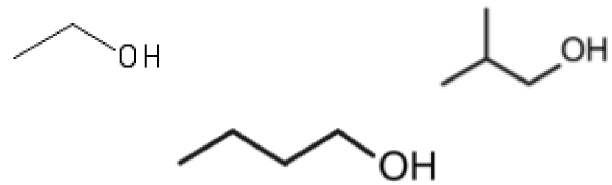
Piston damage by long-term knock (Lawrence Livermore National Laboratory)

More efficient and less polluting spark-ignition (SI) engines
→ Downsizing : same power from reduced volume, but more severe knock is expected!

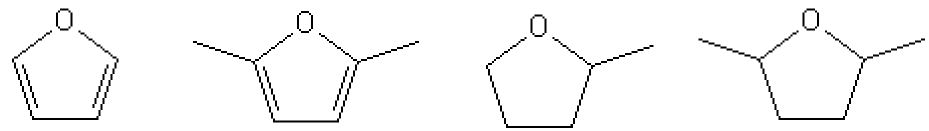
Introduction: Current biofuels for SI engines

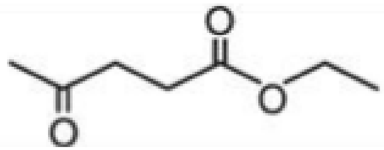
Alcohols

Ethanol, butanol, …

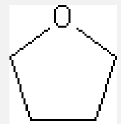
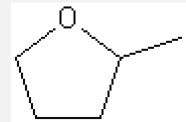
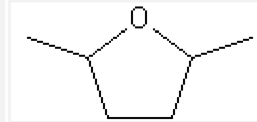
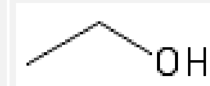


Cellulose-derived oxygenates

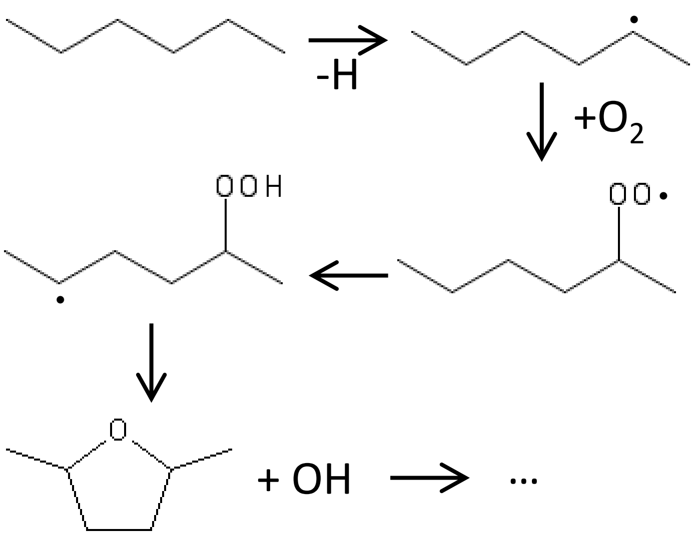




Introduction: Tetrahydrofuran derivatives (THFs)

Molecular structure					
Name	THF	2-MTHF	2,5-DMTHF	Gasoline	Ethanol
Formula	C_4H_8O	$C_5H_{10}O$	$C_6H_{12}O$	mixture	C_2H_5OH
Lower Heating Value (MJ/L)	28.1	28.2	29.5	30–33	21.4
Research Octane Number	73	86	92	88–98	109
Motor Octane Number	65	73	80	80–88	90

Data from:
NREL technical report NREL/TP-5400-50791, 2011
L-S. Tran et al., 8th U.S. National Combustion Meeting, 2013
ASTM Special Technical Publication No. 225, 1958



Low temperature chemistry of n-hexane yielding 2,5-DMTHF during its reaction pathway

THFs are observed during the low-temperature combustion of many hydrocarbons!

Introduction: Objectives of this study

Future of SI engines

- Aggressive turbocharging
- Higher possibility of knocking

Biomass-derived renewable fuels

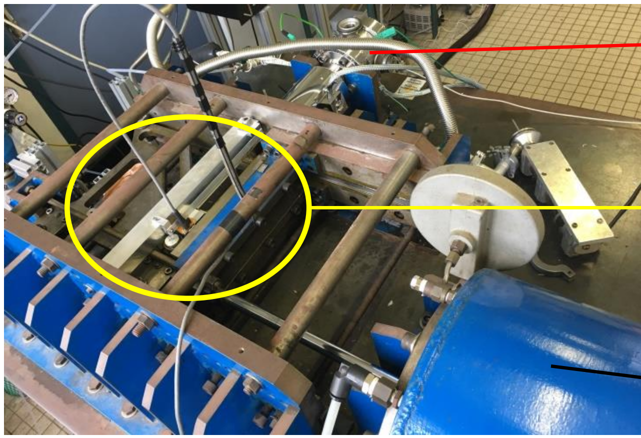
- THFs as gasoline substitutes
- Observed during hydrocarbon combustion

Study the oxidation scheme of THFs via kinetic modeling for better understanding of **autoignition (knocking)** and **species formation (emissions)**

- Ignition delay measurement with **rapid compression machine (RCM)**
- Gas sampling & analyzing with **gas chromatography**

RCM experiments and results

- U.Lille RCM

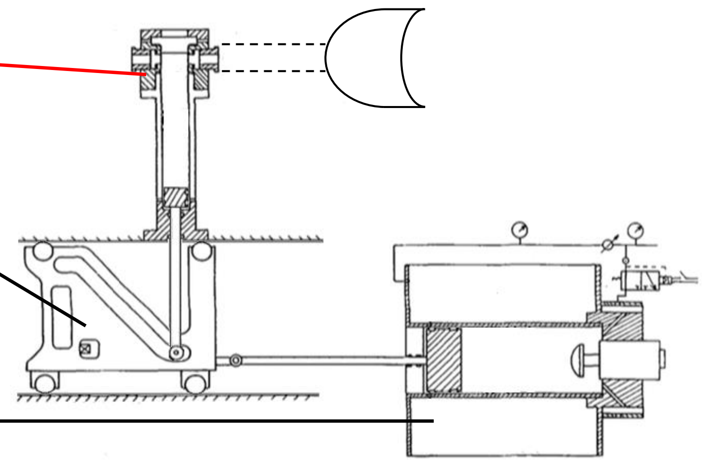


(Sampling canister)

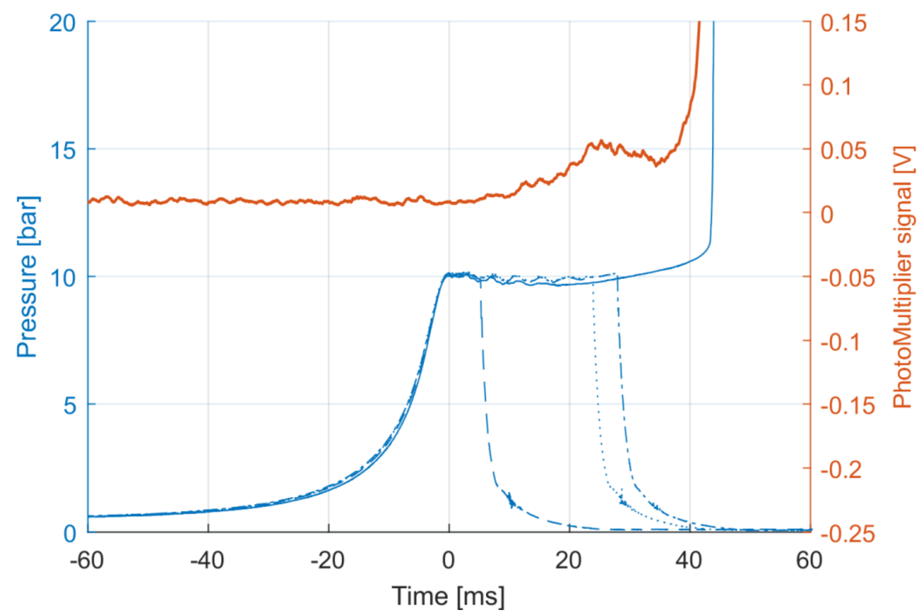
Combustion chamber

Guide cam for piston movement

Air canon for piston driving



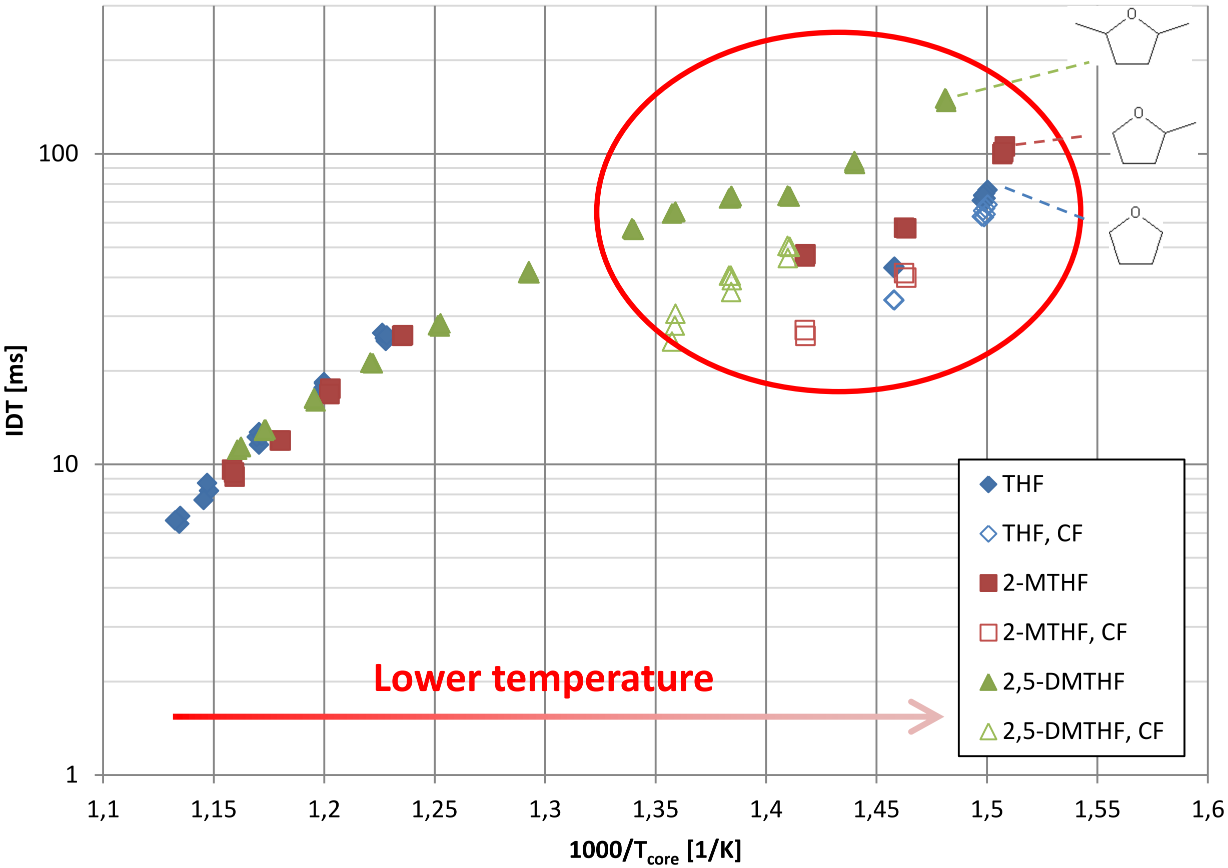
Specifications	
Peak press.	Max. 30 bar
Core gas temp.	600–1000 K
Compression time	60 ms
Sampling	Immediate expansion
Analyzing	GC/MS (TCD, FID)



Autoignition of 2,5-DMTHF/O_2/N_2 at 712 K, 10.1 bar

RCM experiments and results

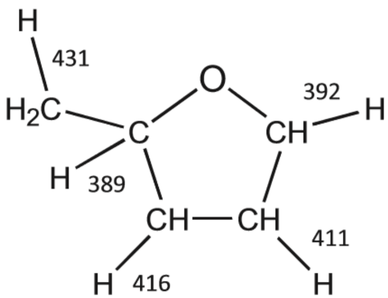
- Ignition delay of THF, MTHF and DMTHF
  - P_{TDC} = 7.5 bar (2,5-DMTHF), 7.5±0.27 bar (THF & 2-MTHF)



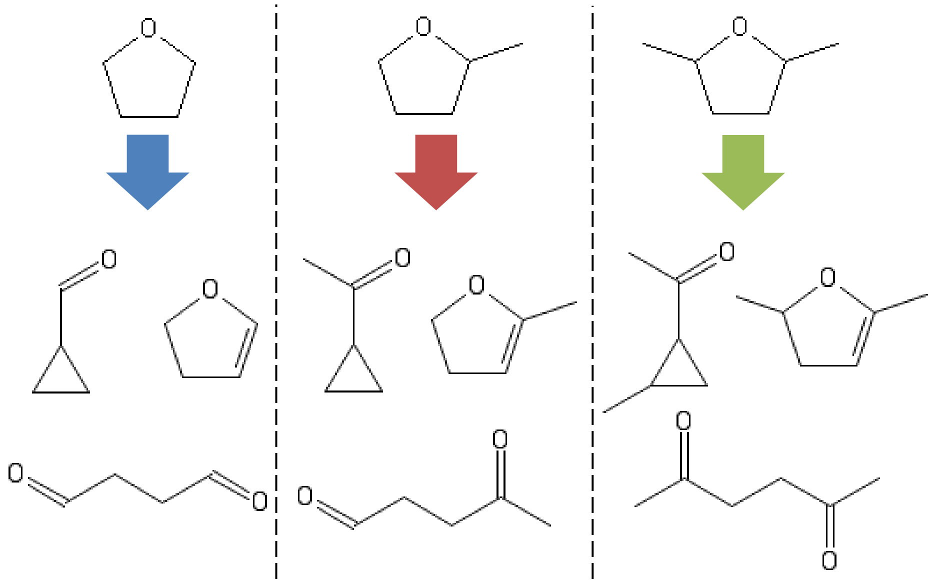
- Negative Temperature Coefficient (NTC) observed
- CF & IDT longer in lower T condition, when methyl groups are added to the basic THF structure
- No significant difference when T > 800 K

Discussion: Specifics of the LTC of THFs

- Preferential reactivity

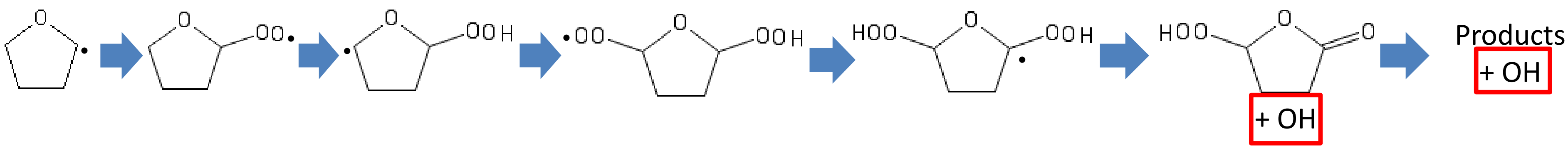


C-H bond dissociation energy (in kJ/mol) of
2-MTHF (J.M. Simmie, J. Phys. Chem., 2016)

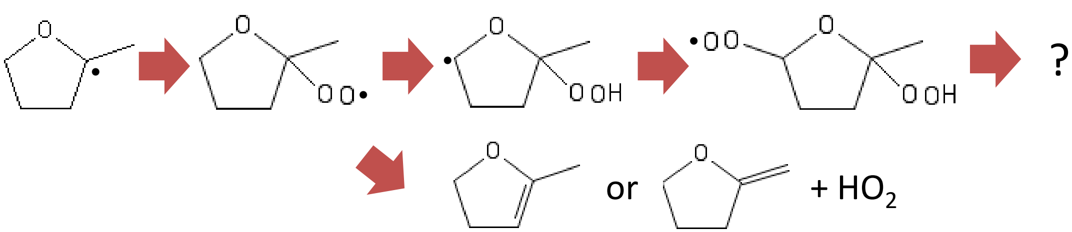


Examples of intermediates during the reaction pathway of THFs

2^{nd} O_2 addition to THF radical: favored pathway with chain branching

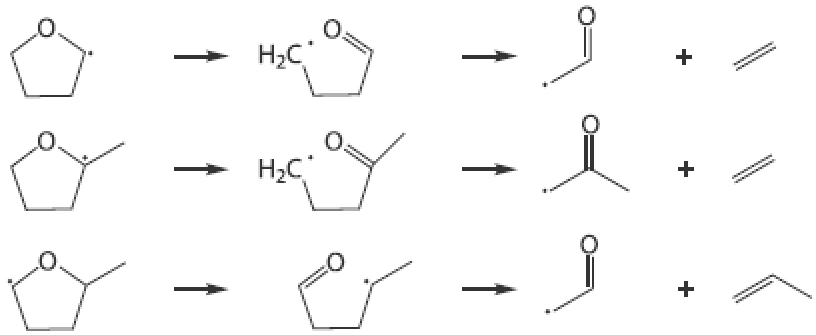


2^{nd} O_2 addition to MTHF: Unfavored pathway

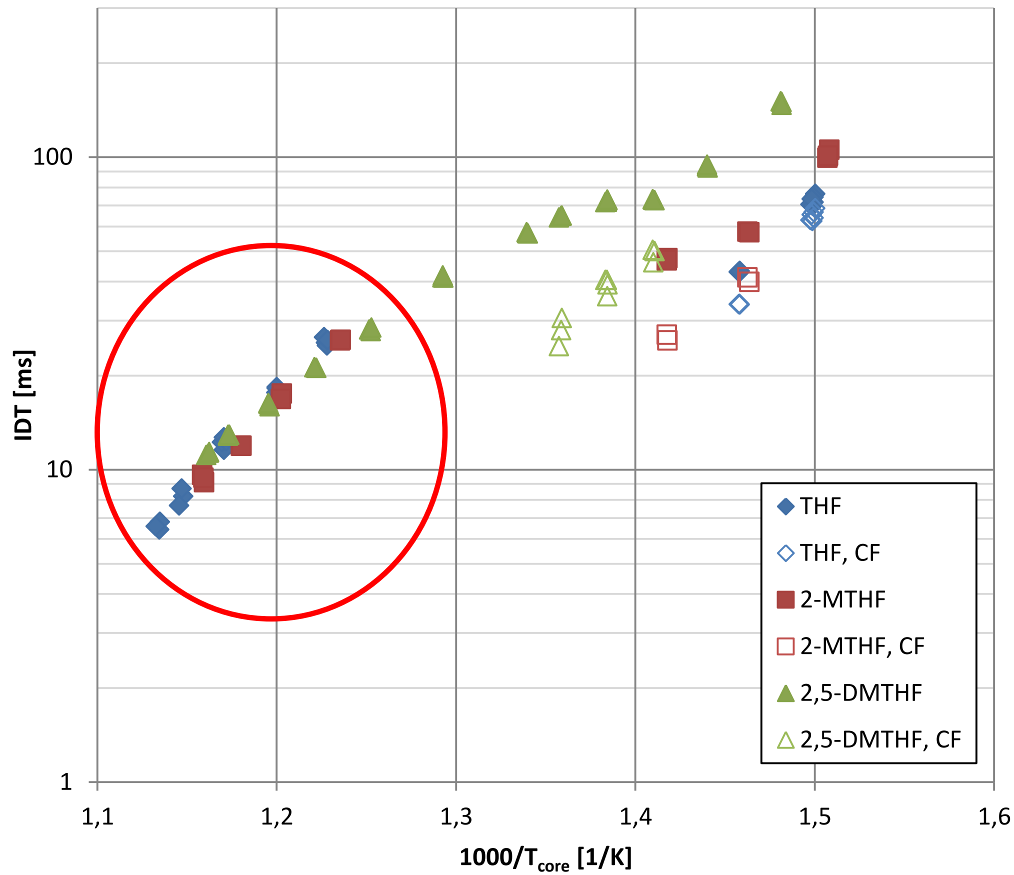


Discussion: How about T > 800 K?

- After H-abstraction, C-O bond dissociates → ring opening



Ring opening of THF and 2-MTHF
(A. Sudholt et al., Proc. Combust. Inst., 2015)



➢ Products after the ring opening have similar reactivity

Conclusions

1. THFs: promising fuel substitutes, and important intermediates of hydrocarbon oxidation

2. Different low temperature reactivity between THFs
   → different reaction pathway after H-abstraction
   → explained by experimental and modeling studies
   → different engine performance (i.e. octane number)

3. Kinetic modeling of 2,5-DMTHF in progress at PC2A

Merci de votre attention!

Q & A