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# A KINETIC MODELING STUDY OF MIXTURES OF METHYL-ESTERS WITH ALCOHOL FUELS

**Chiara Saggese, Giovanni Genova, Roberto Grana, Alessio Frassoldati, Tiziano Faravelli, and Eliseo Ranzi**

*Department of Chemistry, Materials, and Chemical Engineering, Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133 Milano, Italy*

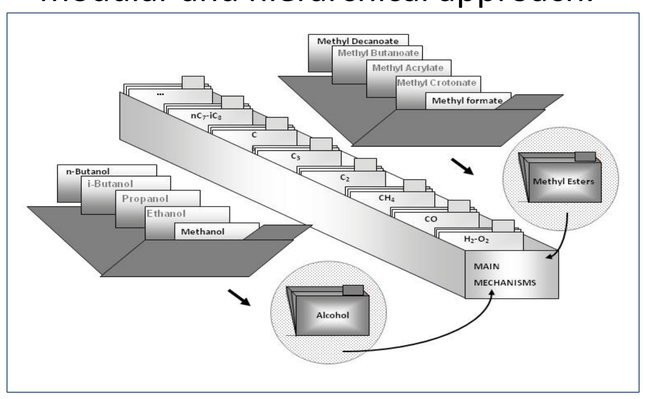
## OBJECTIVE

Aim of this work is to discuss and verify the ability of a lumped kinetic model of methyl-esters to simulate the oxidation and combustion of mixtures of these components with alcohol fuels on a wide range of operating conditions.

## KINETIC SCHEME FEATURES

### Approach

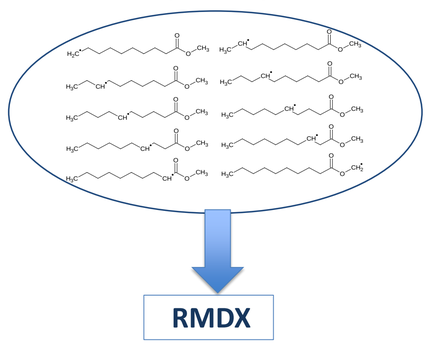
The kinetic scheme is developed with a modular and hierarchical approach.




### Simplification Methods

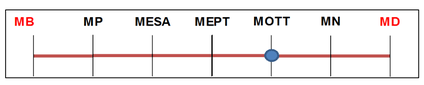
We use the lumped reduction method and the lever rule to decrease the number of species.

**LUMPING**



RMDX

**LEVER RULE**




Methyl octanoate is composed by 1/3 methyl butanoate and 2/3 methyl decanoate mixture

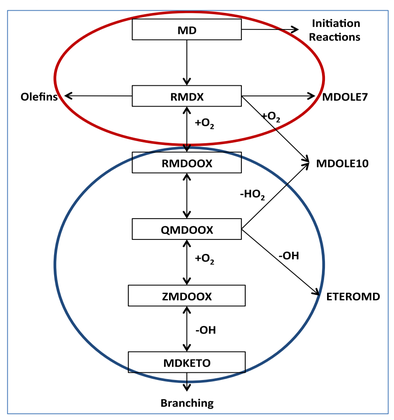
### Pro's

- Kinetic model results more flexible and reliable over a wide range of operating conditions.
- It needs only few species for each fuel.
- The simplified structure permits to decrease the computational effort compared with detailed models .
- It is relativily simple to extend the methyl butanoate kinetic mechanism up to larger methyl esters.

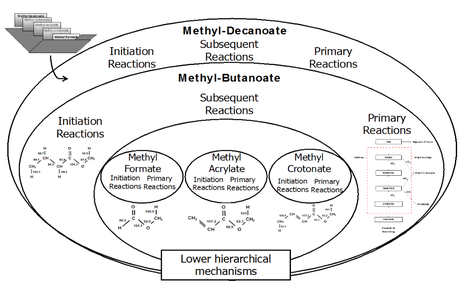
## METHYL DECANOATE'S KINETIC SCHEME

### Development

**PRIMARY SCHEME (extension from MB scheme)**



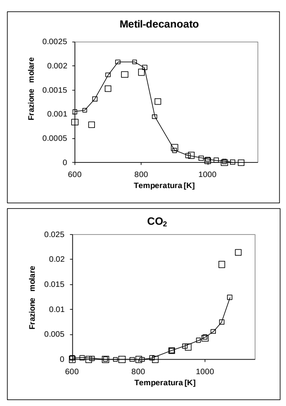

**GLOBAL SCHEME**




**ONLY 12 NEW SPECIES ADDED FOR MD**

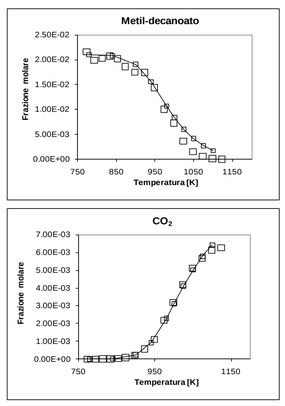
### Wide Range Validation

**OXIDATION**



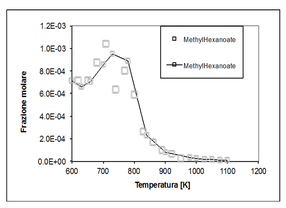

Glaude 2010; JSR; 10 atm; ϕ=1.

**PYROLYSIS**

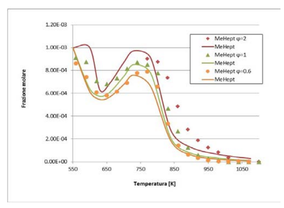



Herbinet 2011; JSR; 10 atm.

**METHYL HEXANOATE OXIDATION (as 2/3 MB and 1/3 MD mixture)**




**METHYL EPTANOATE OXIDATION (as 1/2 MB and 1/2 MD mixture)**




Dayma 2009; JSR; 10 atm.

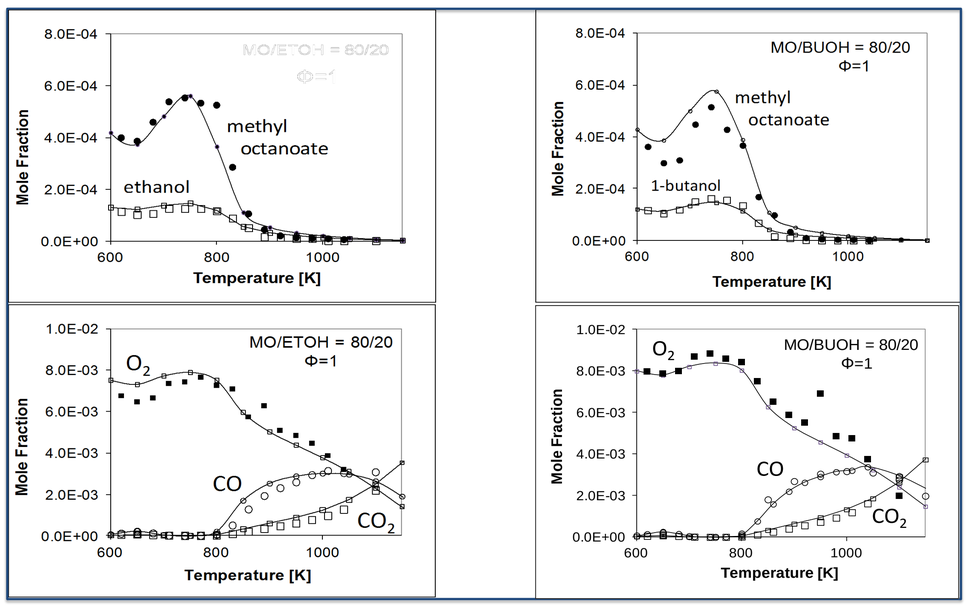
## MODEL VALIDATION ON METHYL ESTERS-ALCOHOLS MIXTURE

**CONDITIONS**: JSR, P=10 atm, τ=0.7 s, T=560-1200 K, ϕ=0.5-2.

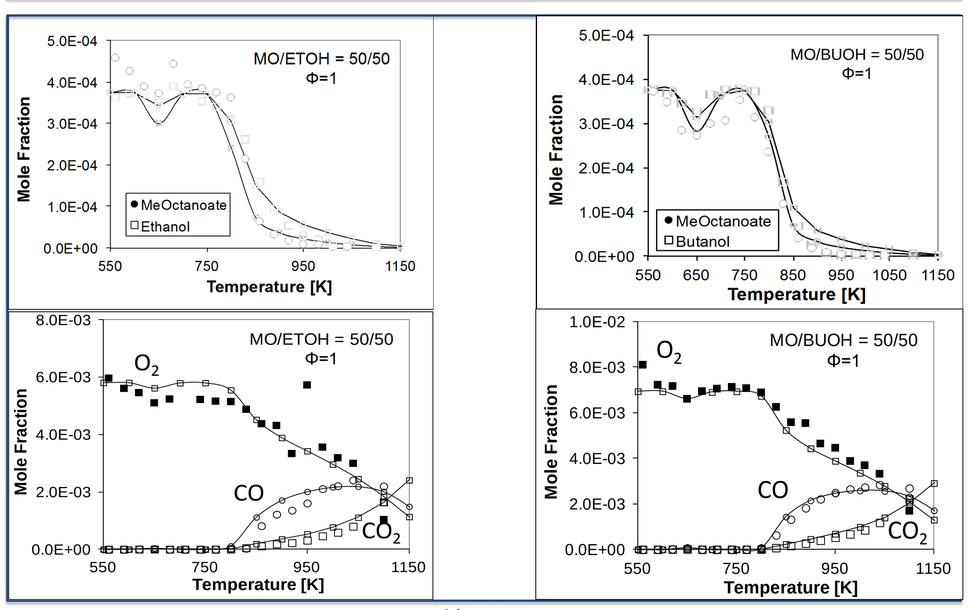
**INLET FUEL: 80/20 and 50/50 Ester/Alcohol, 1% Methyl Ester.**

**Methyl Octanoate-Ethanol** | **Methyl Octanoate-Butanol**

**80/20**




**50/50**




Togbè 2010; JSR; 10 atm.

## CONCLUSIONS

Despite the lumped approach and the use of the lever rule to emulate the combustion behavior of methyl octanoate, the proposed kinetic mechanism generally represents fairly well the experimental measurements of biodiesel-alcohol surrogate fuels. The present validation of the kinetic model of methyl-esters for the intermediate methyl octanoate lays the bases for its reasonable extension to the heavier methyl esters, real bio-fuels components.

[1] C. Togbé, J.-B. May-Carle, G. Dayma, and P. Dagaut 'Chemical Kinetic Study of the Oxidation of a Biodiesel-Bioethanol Surrogate Fuel: Methyl Octanoate-Ethanol Mixtures' J. Phys. Chem. A 2010a, 114, 3896–3908.
[2] C. Togbé, G. Dayma, A. Mzé-Ahmed, and P. Dagaut' Experimental and Modeling Study of the Kinetics of Oxidation of Simple Biodiesel-Biobutanol Surrogates: Methyl Octanoate-Butanol Mixtures' Energy & Fuels 2010b, 24, 3906–3916.
[3] R. Grana, A. Frassoldati, A. Cuoci, T. Faravelli, and E. Ranzi 'A wide range kinetic modeling study of pyrolysis and oxidation of methyl-butanoate and methyl-decanoate. Note I: Lumped kinetic model of methyl-butanoate and small methyl-esters.' (Submitted to Energy, July 2011)
[4] K. M. Van Geem, A.Cuoci, A. Frassoldati, S. P. Pyl, G.B. Marin, E. Ranzi 'An Experimental and Kinetic Modelling Study of Pyrolysis and Combustion of Acetone-Butanol-Ethanol (ABE) Mixtures' MCS7 Cagliari, Italy, September, 2011.
[5] R. Grana, A. Frassoldati, T. Faravelli, U. Niemann, E. Ranzi, R. Seiser, R. Cattolica, K. Seshadri 'An experimental and kinetic modeling study of isomers of butanol' Combustion and Flame 157, (2010), 2137 – 2154.
[6] Dayma G., C. Togbè, P. Dagaut. Detailed Kinetic Mechanism for the Oxidation of Vegetable Oil Methyl Esters: New Evidence from Methyl Heptanoate. 2009, Energy Fuels, Vol. 23, pp. 4254–4268.
[7] Glaude P.A., Herbinet O., Bax S., Biet J., Warth V., Battin-Leclerc. Modeling of the oxidation of methyl esters—Validation for methyl hexanoate, methyl heptanoate, and methyl decanoate in a jet-stirred reactor. F. 2010, Combustion and Flame, Vol. 157, pp. 2035-2050.
[8] Herbinet O., Glaude P.A., Warth V., Battin-Leclerc F. Experimental and modeling study of the thermal decomposition of methyl decanoate. 2011, Combustion and Flame, Vol. 158, pp. 1288-1300.