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MARIE CURIE ACTIONS
MULTISCALE COMPUTATIONAL MODELING OF CHEMICAL AND BIOMEDICAL SYSTEMS

# MicroKinetic Engine (μKE): A tool for (micro)kinetic modelling

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## Objective

**Development of a generic tool "MicroKinetic Engine"[1] for (micro)kinetic modelling of chemical reactions**

## Justification

**High throughput Experimentations**

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**Microkinetic Modeling**
(includes all elementary steps)

↓

1. **Optimize catalyst properties** (pore radius, site density, etc.)
2. **Predict behavior for** *reactions I compounds* **of the same family**

## μKE Features

- Performs microkinetic modeling adopting complex networks of heterogeneous systems
- No programming required by the end user
- Incorporates differential and algebraic solvers + deterministic & stochastic optimization routines
- Able to provide information about quasi-equillibruim steps. Reaction orders can also be estimated
- No rate determining step.
- Provides parity and residual plots along with the statistical analysis of results, e.g. 95% confidence interval, t-value, F value etc.

## Mathematical model

### Objective function

$$S(\beta_j) = \sum_{i=1}^{N_{res}} w_i \sum_{l=1}^{N_{exp}} \left(F_{il}^{calc} - F_{il}^{\exp}\right)^2 \xrightarrow{\beta_j} minimum$$

### Reactor model

$$\frac{dF_i}{dW} = R_i \quad , \quad i = 1...N_{responses}$$ ⇐ Batch, PFR

$$\frac{d(V \cdot C_i)}{dt} = F\left(C_i^{in} - C_i\right) + R_i,$$ ⇐ SBR

$$F_i^{in} - F_i^{out} + R_i w_{cat} = 0$$ ⇐ CSTR

### Kinetic model

$$r_s = k_s p_{response}^n \theta_{intermediate}^m C_{tot} \quad , \qquad s = 1...N_{elem\_steps}$$

$$k_s = f(\beta_j), \qquad j = 1...N_{parameters}$$

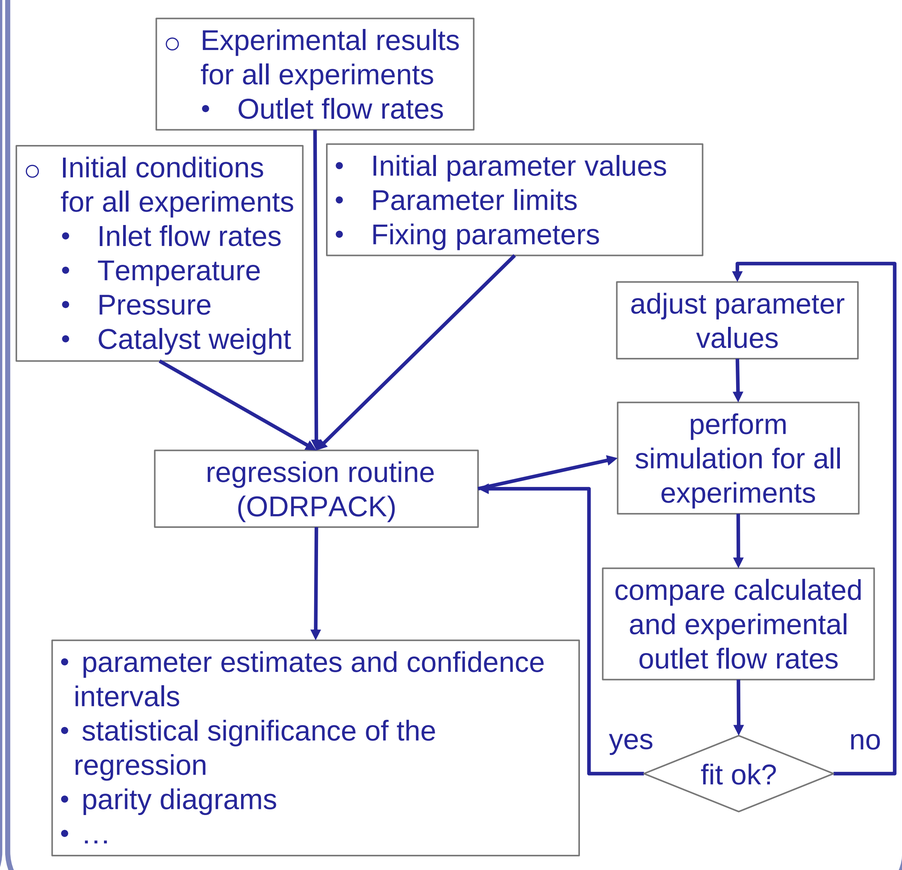
### Non-isothermal parameter estimation using Arrhenius equation

$$k_s = k_{avg} \cdot exp\left(-\frac{E_{act}}{R}\left(\frac{1}{T} - \frac{1}{T_{avg}}\right)\right)$$

- Mass balance for the catalyst's active sites
- Intermediates are more reactive than reactants and products, i.e. net rate of formation equals zero

## Graphical user interface


## μKE work flow

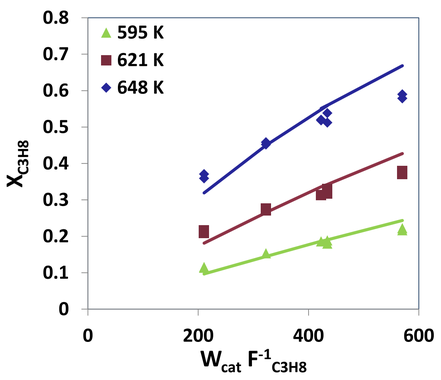



## Case study

### Power law

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

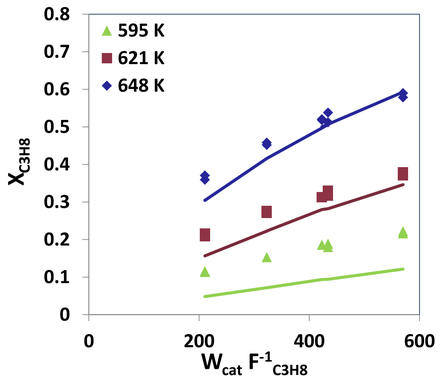
- Power law reaction kinetics
- Reaction orders estimated
- Data taken from the work performed at the lab by Heynderickx et al[2]




### Reaction mechanism elucidation

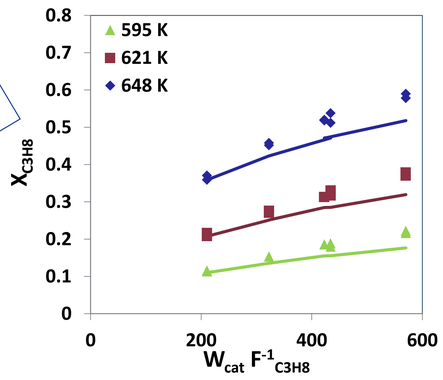
$$C_3H_8 + * \rightleftharpoons C_3H_8*$$
$$C_3H_8* + 5O_2 \rightarrow 3CO_2 + 4H_2O + *$$

- $C_3H_8$ adsorbs on the catalyst surface and then reacts with $O_2(g)$ forming products in gas phase
- Underlying chemistry is reflected in the performance curves




$$C_3H_8 + * \rightleftharpoons C_3H_8*$$
$$O_2 + * \rightleftharpoons 2O*$$
$$C_3H_8* + 10O* \rightarrow 3CO_2* + 4H_2O* + 4*$$
$$CO_2* \rightleftharpoons CO_2 + *$$
$$H_2O* \rightleftharpoons H_2O + *$$

- Reactants adsorption is followed by the surface reaction and the finally the products are desorbed
- Surface reaction is the slowest non-equilibrated step. Hence rate determining step.
- Trends are in agreement with the published data[2]




| k(avg) | Estimated values | Activation energies | Estimated values (kJ/mol) |
|---|---|---|---|
| $k_{C_3H_8}^{fwd}$ | 4.24±2.29 kPa$^{-1}$s$^{-1}$ | $E_{C_3H_8}^{fwd}$ | 1.26±0.51 |
| $k_{C_3H_8}^{rev}$ | (1.11±0.46)x10$^{+08}$ s$^{-1}$ | $E_{C_3H_8}^{rev}$ | 23.3±15.0 |
| $k_{O_2}^{fwd}$ | 4.22±1.73 kPa$^{-1}$s$^{-1}$ | $E_{O_2}^{fwd}$ | 0.399±0.11 |
| $k_{O_2}^{rev}$ | (7.87±4.41)x10$^{+07}$ s$^{-1}$ | $E_{O_2}^{rev}$ | 13.7±5.3 |
| $k_s$ | (5.61±2.23)x10$^{+11}$ $kg_{cat}$mol$^{-1}$s$^{-1}$ | $E_s$ | 124.0±21.0 |
| $k_{CO_2}^{rev}$ | (2.27±1.49)x10$^{+01}$ s$^{-1}$ | $E_{CO_2}^{rev}$ | 74.9±51.4 |
| $k_{CO_2}^{fwd}$ | (2.00±0.88)x10$^{+01}$kPa$^{-1}$s$^{-1}$ | $E_{CO_2}^{fwd}$ | 1.37±0.66 |
| $k_{H_2O}^{rev}$ | (2.05±1.15)x10$^{+01}$ s$^{-1}$ | $E_{H_2O}^{rev}$ | (79.5±28.6 |
| $k_{H_2O}^{fwd}$ | (3.09±1.10)x10$^{+01}$ kPa$^{-1}$s$^{-1}$ | $E_{H_2O}^{fwd}$ | 0.70±0.55 |

Total active site concentration : 1.204421 ± 0.00846 mol/$kg_{cat}$

### Other case studies

- Toluene hydrogenation
- Oxidative coupling of methane
- Methane aromatization
- n-hexane hydrocracking

## Conclusion

- Kinetic modelling based on user defined reaction network
- Top-down methodology proved to be helpful in using the Microkinetic engine (μKE)
- A priori knowledge can be used to reduce number of parameters to be estimated.
- Significant estimation + physical meaning for the kinetic parameters of the microkinetic model

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## References

1. Metaxas, K., J. Thybaut, G. Morra, D. Farrusseng, C. Mirodatos and G. Marin (2010). Topics in Catalysis 53(1-2): 64-76.
2. Heynderickx, P., J. Thybaut, H. Poelman, D. Poelman and G. Marin (2010). Applied Catalysis B-Environmental 95(1-2): 26-38.