EUROKIN

Excellence in commercial reaction kinetics

Centre of excellence in reaction kinetics in the industrial and academic world

ISCRE-22 slide show, September 3-5, 2012

Demo version: duration 11 minutes (19 slides)

Origin and ideas of Eurokin

Based on a 1996 industrial survey that revealed a need for improvement in kinetic research

A.N.R. Bos, L. Lefferts, G.B. Marin, M.H.G.M. Steijns, Kinetic research on heterogeneously catalysed processes: A questionnaire on the state-of-the-art in industry, Appl. Catal. A: General 160 (1997) 185-190.

- Gathering of kinetic data, currently very costly and time consuming
- Software for parameter estimation from kinetic data, with an emphasis on user-friendliness

General aims:

1) Implementation of best practise in the area of chemical reaction kinetics in the industrial environment
2) Produce a pre-competitive toolkit for kinetic research

- Faster, cheaper, better reaction rate expressions
- Enabling faster-to-market development and more accurate reactor designs

Eurokin was founded in Summer 1998

The consortium is 100% funded by member companies

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Eurokin consortium

Industrial consortium members

Academic participants in projects

CPE LYON

CPERI

UNIVERSITEIT GENT

Aix*Marseille université

HERIOT WATT UNIVERSITY

NTNU

IRCELYON

INSA ROUEN

National Technical University Athens

NORTHWESTERN UNIVERSITY

QUAECUMQUE SUNT VERA

1851

TUM

UNIVERSITAS CATHOLICA LOVANIENSIS SEDES SAPIENTIAE 1425

POLITECNICO MILANO

TU Delft

Vrije Universiteit Brussel

UCL

UNIVERSITY OF CAMBRIDGE

UCL

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Eurokin membership

- Rolling programme without fixed termination date
- Programme is updated each year, and depends on the priorities of the industrial members
- 3 times per year workshop and Main Committee meeting
- Industrial members pay yearly fee (currently € 12,500)
- Academic members provide support and guidance in the development and execution of the programme
- Confidentiality agreement concerning foreground and background information and knowledge
- All members are allowed to use all tools and reviews

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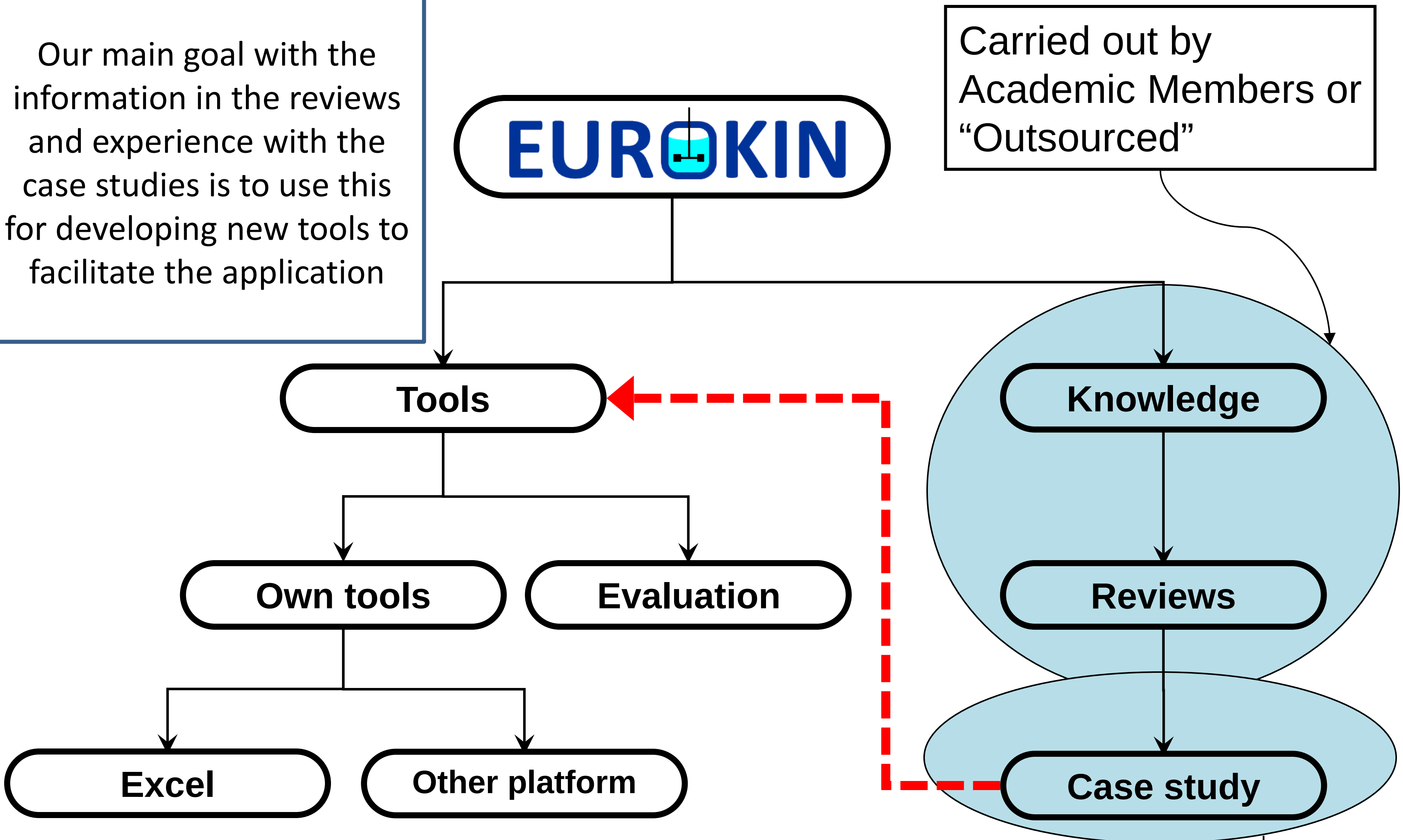
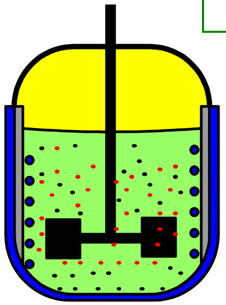
Eurokin ‘Ways of Working’

Our main goal with the information in the reviews and experience with the case studies is to use this for developing new tools to facilitate the application



What have we done up to date ?



(1) Experimental set-up

- Reactor selection for reaction kinetics experiments
- Suppliers of reactor set-ups (also for HTE)

- Assessment of transport limitations (spreadsheets)

Fixed bed reactor
Agitated reactors
Slurry reactor
Robinson-Mahoney reactor
Trickle-bed reactor
Fluidized-bed reactor

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What have we done up to date ?

(2) Kinetic data analysis

- Comparison of software packages for kinetic parameter estimation
- Application of sequential experimental design for kinetic model discrimination and parameter accuracy
- Perturbation / extrapolation
- Coping with irreducible transport phenomena

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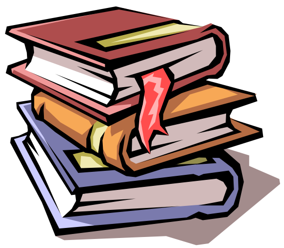
What have we done up to date ?



(3) State-of-the art reviews and case studies

- **Non-experimental methods for estimating reaction rate parameters**
- **Reaction networks and lumping for complex systems**
- **Analysis techniques for petroleum fractions**
- **Estimating liquid-phase reaction kinetics based on gas-phase experimental data** (non-ideality, solvent effects)
- **Effective diffusivity in porous materials** (characterization, models)
- **Kinetics and models for catalyst decay and catalyst regeneration**
- **Extraction of kinetics from large datasets** (plant and HTE)
- **Coupling chemical kinetics with computational fluid dynamics**
- **Non-steady state methods for estimating reaction rate parameters**

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Current programme

- **Category A – Theoretical methods to obtain kinetics**
  - Assessment of non-experimental methods and software by means of case studies of specific reaction network
  - Liquid-phase kinetics
  - Hydrocracking kinetics
- **Category B – Experimental methods and reactors to obtain kinetics**
  - Spreadsheets for evaluating absence of transport phenomena
  - Phase (dis)appearance in GLS reactors
  - Alternative GLS reactors: spinning-disc reactor
  - Thermocouple 'error'
  - Reactors for fast exothermic reactions
  - Mixing for fast reactions
  - Structured catalysts and reactors
  - Methods and approaches for describing the diffusivity in catalyst bodies
  - Reacting particles in fluidized bed reactors
  - Dynamic methods
  - Non-thermal reactors
  - FCC heavy feedstocks and catalyst deactivation
  - In-situ spectroscopy
  - Best experimental practice
- **Category C – Software to obtain kinetics from experimental data**
  - Parameter estimation: objective function, data reconciliation
- **Category D – Implementation of kinetics**

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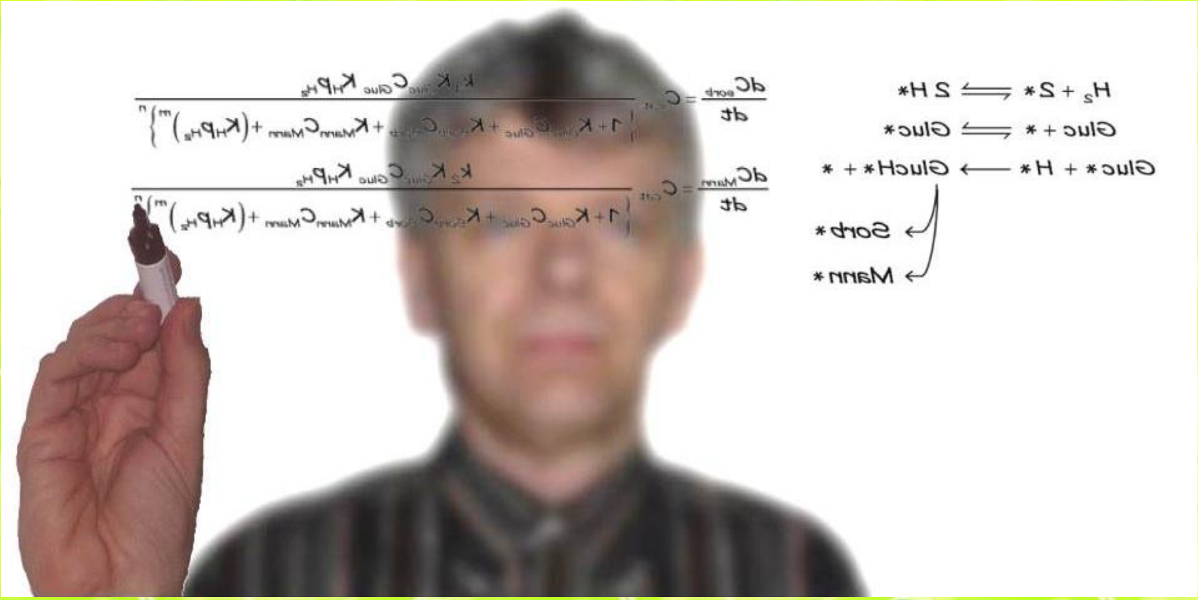
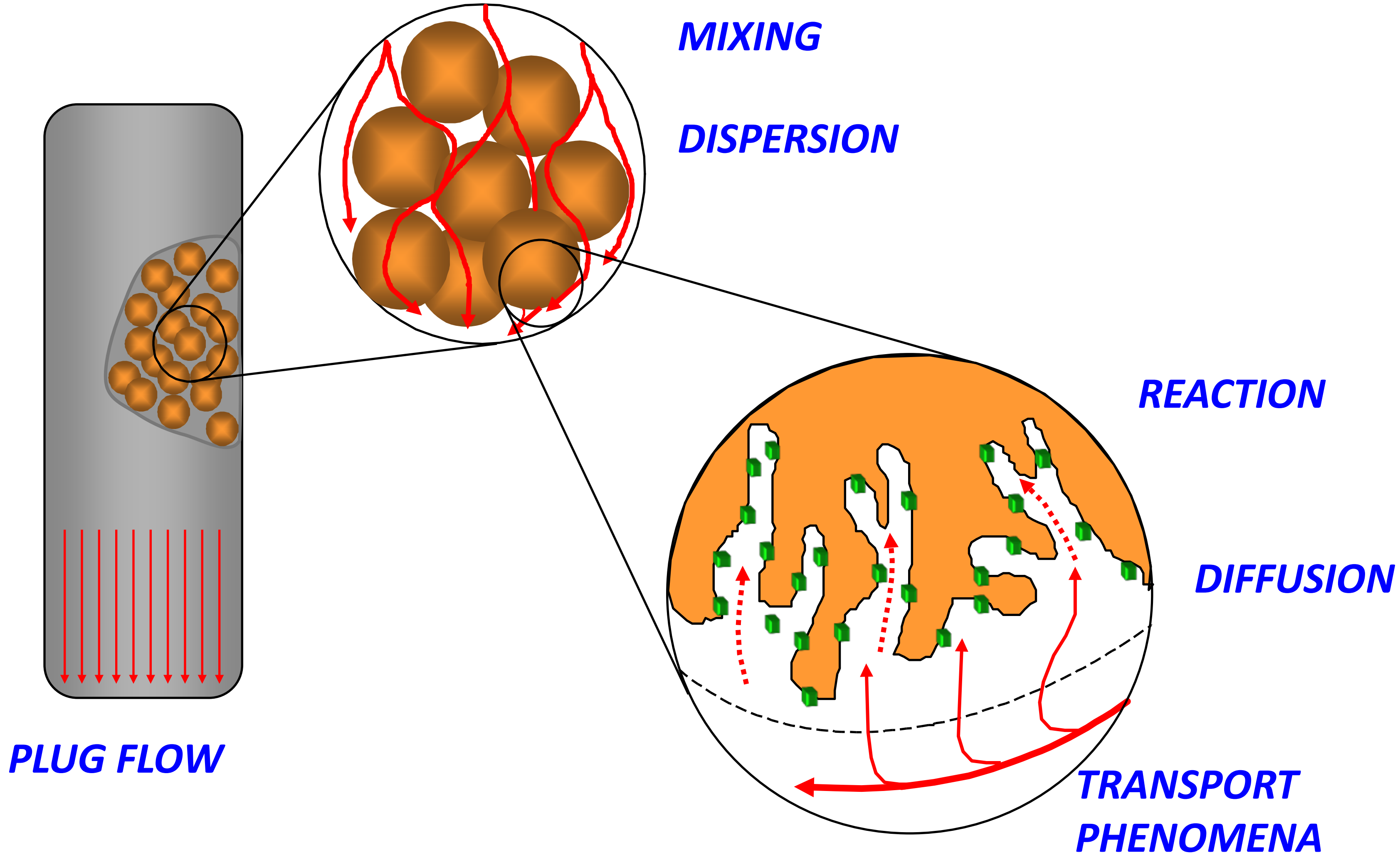
(new) Public Eurokin website



- Public Eurokin website:
  - New public website
  - Modern appearance
  - Information about the consortium and all members
  - All non-confidential workshop presentations
  - Fixed-bed web tool
  - Search function
  - Counters for downloads

➡ (New) Eurokin public website (http:// www.eurokin.org)

Freeware tool: Spreadsheet for assessment of transport limitations in the fixed-bed reactor



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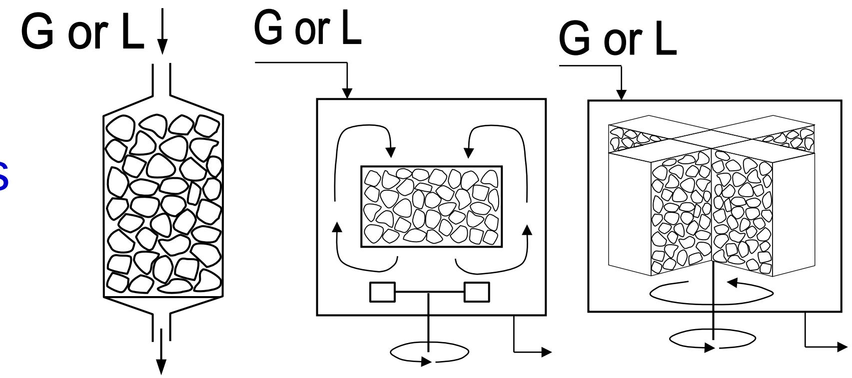
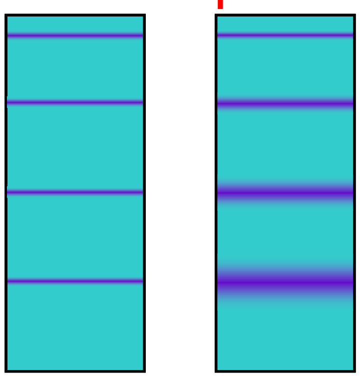
Freeware tool: fixed-bed reactor spreadsheet



Correlations implemented

- ***Gas-solid*** and ***liquid-solid*** fixed beds
- **Needed:** experimental conditions, catalyst and fluid properties
- Calculation if ***intrinsic*** kinetics is measured

- Axial dispersion

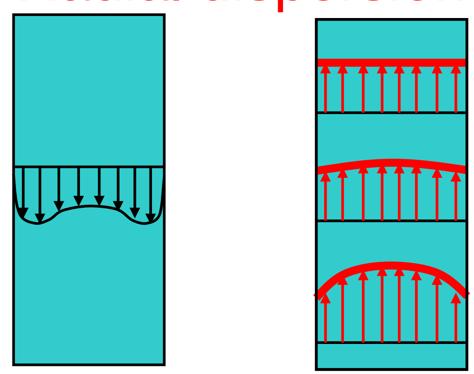


Plug flow | Axial dispersion

Mears (1971):

$$\frac{L}{d_p} > \frac{8}{Bo} n \ln\left\{\frac{1}{1-X_A}\right\}$$

- Radial dispersion :



Velocity profile | Radial temperature gradient

Mears (1971):

$$\frac{d_t}{d_p} > 8$$

Berger & Kapteijn (2007):

$$\ln\left\{\frac{1}{1-X_A}\right\} < a + \frac{b}{Pe'}$$

$$Pe' = \frac{u_0}{4L} \cdot \frac{d_t^2}{D^0_{rad,A}}$$

$$a,b = f\left(\frac{d_t}{d_p}\right)$$

Mears D.E., *Chem. Eng. Sci.* **26** (1971) 1361

Berger, R.J., Kapteijn, F., *Ind. Eng. Chem. Res.* **46** (2007) 3871

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Freeware tool: fixed-bed reactor spreadsheet

Spreadsheet screenshots: input data (1)

EUROKIN SPREADSHEET FOR ASSESSMENT OF TRANSPORT LIMITATIONS IN GAS-SOLID FIXED BEDS

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This webtool is a spreadsheet for selecting proper conditions in a gas-solid fixed-bed reactor for intrinsic reaction kinetics.
It was developed by the Eurokin consortium (http://www.eurokin.org) and made accessible to the public for free in 2012.
It consists of this spreadsheet and a document with background information *EUROKIN_fixed-bed_html_guide.pdf*.

1) Enter feed components and composition

2) Enter components properties

Input

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Feed composition (mol %)	Name	[mol-%]	
Limiting reactant (= "A")	N2O	0.04	(1)
Second compound	O2	0	
Third compound	N2	0	
Dilution (or 4th compound)	He	99.96	

	Reaction (1) stoichiometry	Mol. weight [kg/mol]	Diffus. volume [m^3/mol] (15)
N2O	-1	0.04401	3.59e-5
O2	0.5	0.032	1.66e-5
N2	1	0.02802	1.79e-005
He	0	0.004	2.88e-006
	Mixture value :	**0.004016**	

3) Enter physical properties of gas mixture

Physical properties of the components

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General physical properties	(mixture values)	
Heat capacity	20.8000	[J/mol K]
Viscosity	2.992e-005	[kg/m s]
Thermal conductivity	0.227050	[W/m K]
(The user should adapt these values accordingly)		

Calculation of Diffusion coefficient		(15)
D(N2O-O2) =	1.715e-5	[m^2/s]
D(N2O-N2) =	1.745e-5	[m^2/s]
D(N2O-He) =	5.918e-5	[m^2/s]
D(N2O),m Wilke eq. =	5.918e-5	[m^2/s]
Do(N2O),m =	5.910e-5	[m^2/s]
f(N2O),app =	1.0002	
Bulk diffusivity: D(N2O),m =	5.909e-5	[m^2/s]
Knudsen diffusivity: D_K(N2O) =	2.057e-6	[m^2/s]

4) Calculation of the diffusivity

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Freeware tool: fixed-bed reactor spreadsheet

Spreadsheet screenshots: input data (2)

4) Specify reaction conditions

Reaction conditions:			
Catalyst temperature	550	[K]	(1)
Total pressure	250	[kPa]	
Total molar inlet flow	0.000132	[mol/s]	

5) Specify catalyst + dilution properties

Properties of catalyst and dilution			
Amount of catalyst	0.05	[g]	
Amount of bed dilution	0.15	[g]	
Catalyst pellet diameter	0.4	[mm]	
Bed porosity	0.4	$[m^3/m^3_{bed}]$	(2)
Cat. internal specific area	122	$[m^2/g]$	
Catalyst pellet porosity	0.6	$[m^3/m^3_{pellet}]$	
Catalyst bulk density	984	$[kg/m^3_{bed}]$	
Catalyst pellet tortuosity	4	[-]	
Cat. pellet thermal conduct.	0.5	[W/mK]	
Dilution pellet density	3200	$[kg/m^3_{pellet}]$	
Dil. pellet thermal conductivity	40	[W/mK]	

6) Specify reactor dimensions

Reactor dimensions:		
Internal reactor diameter	4	[mm]
Diameter thermowell	0	[mm]

7) Specify reaction character-istics and observed rate

Reaction rate			
Observed reaction rate	0.0001	[mol-A/kg-cat.s]	(1)
Reaction order A	1	[-]	
Apparent activation energy	150	[kJ/mol-A]	
Reaction enthalpy	81.5	[kJ/mol-A]	

Calculated values		
Volumetric flow at reaction cond.	2.414e-6	$[m^3/s]$
Volumetric flow at STP	1.776e+2	[ml/min]
Superficial velocity	0.19213	[m/s]
Particle Reynolds number	0.56397	
Density mixture	0.21956	$[kg/m^3]$
Molar volume	1.83e-2	$[m^3/mol]$
Pr	0.68251	[-]
Sc	2.30627	[-]
Space time $[W_{cat}/(mol\text{-}A/s)]$	9.470e+2	[kg/s mol]
Weight dilution degree	0.75000	$[kg_{dil}/(kg_{cat}+kg_{dil})]$
Volume dilution degree	0.60591	$[m^3_{dil}/(m^3_{cat}+m^3_{dil})]$
Bed cross-sectional area	1.257e+1	$[mm^2]$
Bed height	1.026e+1	[mm]
Real residence time in bed	2.136e-2	[s]
Total catalyst bed volume	1.289e+2	$[mm^3]$
Catalyst pellet density	1640.00	$[kg/m^3]$
Average pore radius	5.998	[nm]
Catalyst solid density	4100.00	$[kg/m^3]$
Catalyst pore volume	0.36585	[ml/g]
Average pellets thermal cond.	1.2448	[W/m K]
Observed rate constant	1.000e-6	$[mol\text{-}A/kg\text{-}cat.s.Pa\text{-}A^n]$
Reaction rate per pellet volume	1.640e-1	$[mol\text{-}A/m^3_{pellet}\ s]$
Conversion of A	0.09035	(3)

8) Check calculated values; the conversion can be used to find the observed reaction rate

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Results concerning transport limitations and other disturbing phenomena

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Pressure drop over the catalyst bed (4)

Friction factor	1512.49		
Pressure drop over the bed	314.46	[Pa]	
ΔP/P ratio	1.258e-3	; must be < (0.2/n) =	0.200
Criterion OK			

Conditions for the maximum bed dilution (7)

Relative deviation (Δ)	2.708e-3	
Maximum allowed b	0.966	[vol-dil/vol-tot]
Experimental b	0.606	
Criterion OK		

External mass transport limitation (8)

Sh	3.031	[-]
Mass transfer coefficient (k_g)	0.44768	[m^3/m^2s]
$a_v = 6/d_p$	1.500e+4	[m^2/m^3-pellet]
C(N2O),bulk	2.187e-2	[mol/m^3]
Ca	1.117e-3	; must be < 0.05/n
Efficiency (for n = 1)	0.99888	[-]
Criterion OK		

Radial heat transfer limitation (11)

Pe_{rf}	10.3281	[-]	
$\lambda_{er,0}/\lambda_G$	4.2266	[-]	
$\lambda_{er,conv}/\lambda_G$	0.0373		
λ_{er}	0.9681	[W/mK]	
Pr (air, 80°C)	0.6850		
$\alpha_{w,0}$	2694.0799	[W/m^2 K]	
$\alpha_{w,conv}$	28.1102	[W/m^2 K]	
α_w	2722.1901	[W/m^2 K]	
| ΔT(rad) |	1.6323e-3	[K]; must be <	0.838
Criterion OK			

If the temperature of the wall is measured instead of the temperature at the central bed axis, **another criterion** applies: (11)

| ΔT(rad) |	2.7933e-3	[K]; must be <	0.838
Bi_{wall}	11.2474	[-]	
Criterion OK			

Conditions for allowing assumption ideal plug flow behaviour

Axial dispersion (5)

Bo (=Pe_p)	1.4399	[-]
Constant in criterion	8	
h_{bed}/d_p (minimum required)	0.526	
h_{bed}/d_p (experimental)	25.651	
Criterion OK		

Radial dispersion (6)

Criterion: d_t/d_p should be at least	8
d_t/d_p	10.00
Criterion OK but close to limit	

Internal diffusion limitation (9)

D(eff.)N2O	2.981e-7	[m^2/s]	
Weisz modulus (Φ)	0.11179	; must be <	0.08
Approximate Thiele modulus (ϕ)	0.33435	[-]	
tanh (3ϕ)	0.76288	[-]	
Approximated efficiency (η)	0.93876	[-]	
Criterion NOT OK			

External heat transport limitation (10)

Nu	2.6868	[-]	

Note that Nu may get as low as 0.1 at Re <1 in case of channeling !

Heat transfer coefficient $\alpha_p = h_w$	1525.11	[W/m^2 K]	
| ΔT(film) |	5.843e-4	[K]; must be <	0.838
Criterion OK			

Temperature gradient within the pellet (12)

The effect of the internal temperature gradient on the net production rate is smaller than 5% if :

| ΔT(int) |	7.129e-5	[K]; must be <	0.838
Criterion OK			

Adiabatic temperature rise (ΔT_{ad}) (13) (14)

ΔT(ad)	0.14161	[K]

Reset | Print | http://www.eurokin.org/

Freeware tool: fixed-bed reactor spreadsheet

Results

9) Check the results and see whether transport limitations are significant or not.

All criteria should be ‘OK’

10) You may start ‘playing’ with the input conditions, such as particle size and conversion, to fulfil all the criteria

11) You may print the results using the print button

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General recommendations for kinetics research (1)

- The experimental reactor should not be a small-scale copy of the industrial reactor
- Search for information on comparable chemical systems
- Determine in advance which kinetic data you really need
- Check for reproducibility by performing replicate experiments
- Start to carefully analyze your data for reaction sequence and influence of components as early as possible (already during the experiments and certainly before starting modeling)
- Use more theoretically based models if extrapolation is required
- Define several kinetic models and model selection criteria

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General recommendations for kinetics research (2)

- Use LHHW type rate expressions for heterogeneously catalyzed reactions (+ elementary surface reactions)
- Reduce correlations between adsorption constants by performing experiments with (co-)feeding intermediates or reaction products
- Decouple k_0 and E_{act}
- Check for significance of the parameters (i.e. confidence range smaller than parameter value) *(t-value)*
- Check for adequacy of the model *(F-test)*
- Apply experimental design for model selection and improvement of parameter accuracy

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Resume

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- **Excellence centre in reaction kinetics in the industrial and academic world**
- **Consortium with currently 9 industrial members aiming at:**
  1) **Development of handy tools applicable in the industrial research**
  2) **Scientific reviews by acknowledged academic centres on industrially relevant subjects somehow related with reaction kinetics today as well as in the future**