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FACULTY OF ENGINEERING

Robinson-Mahoney reactors as a tool for assessing multi-phase kinetics at laboratory scale

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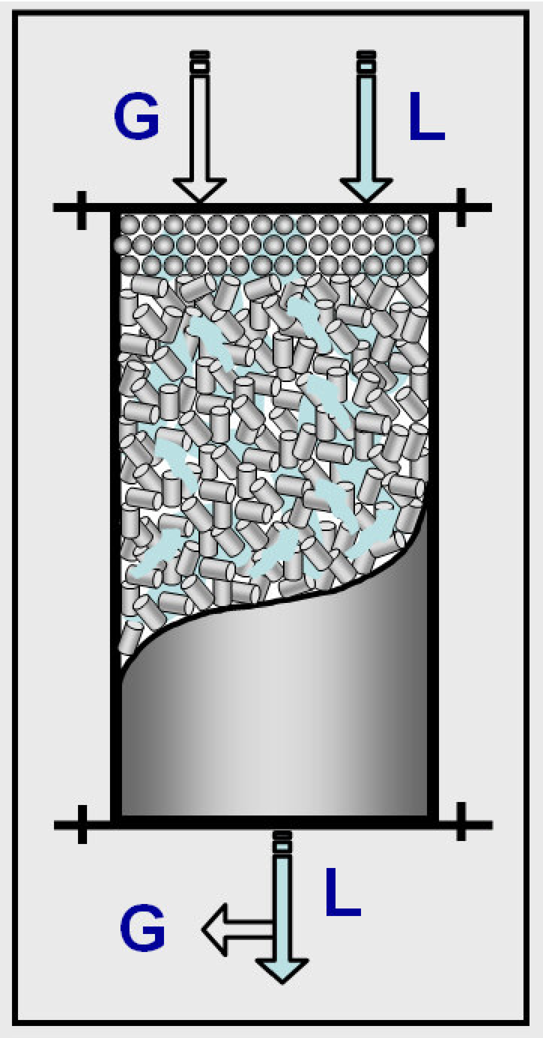
http://www.lct.UGent.be

IDECAT
Integrated Design of Catalytic Nanomaterials for a Sustainable Production

solid catalysts in gas-liquid mixtures

- hydroprocessing / refining
  - hydrocracking
  - hydrodesulphurization
  - aromatic hydrogenation
- fine chemicals
  - hydrogenation reactions
  - …

industrial operation



- trickle bed reactors
  - fixed catalyst bed
  - cocurrent down flow of the gas and the liquid phase
  - adiabatic reactor
  - high temperature
  - high pressure

lab scale testing

plug flow reactors

- advantages
  - ease of construction
  - ease of operation
- disadvantages
  - flow pattern ideality difficult to realize
  - mass transport limitations more likely

mixed flow reactors

- advantages
  - flow pattern ideality
  - avoiding mass transport limitations
- disadvantages
  - long stabilization times
  - moving equipment

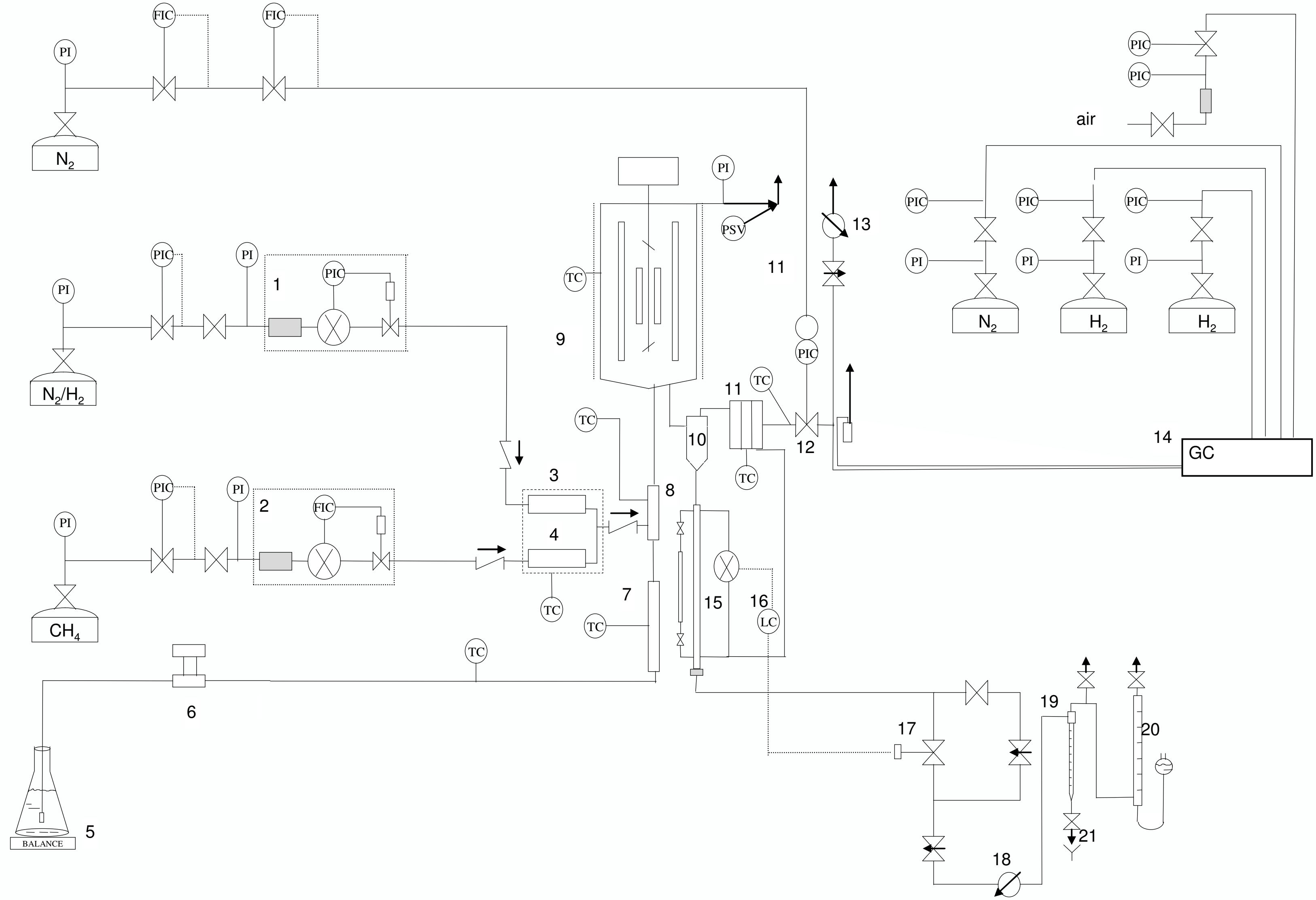
plug flow: practical reasons

mixed flow: fundamental reasons

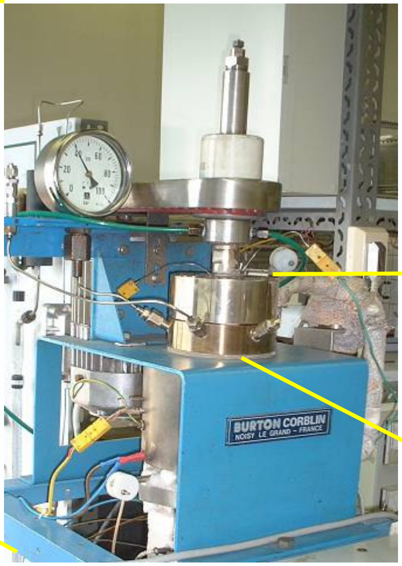
the Robinson-Mahoney reactor

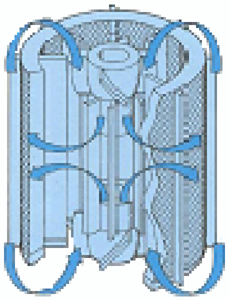
- experimental set-up
- reactor description
  - flow pattern
  - outlet configuration
  - residence time
- effluent section
  - gas-liquid separation
  - measurement outlet flow rates
- gas/liquid composition
  - phase equilibrium
  - individual phase composition
- example

scheme experimental set-up



experimental set-up





'live' view experimental set-up

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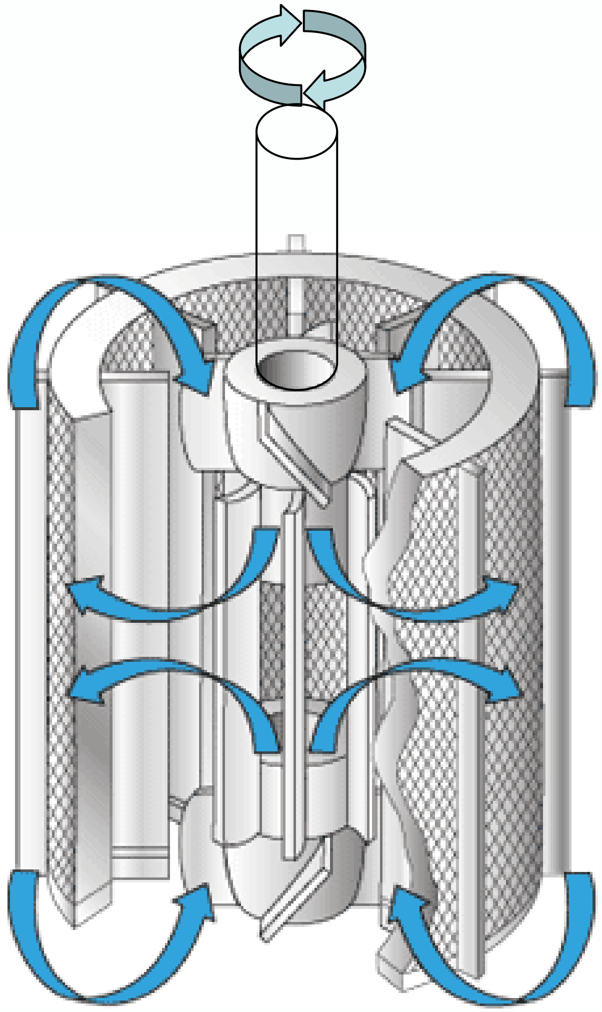
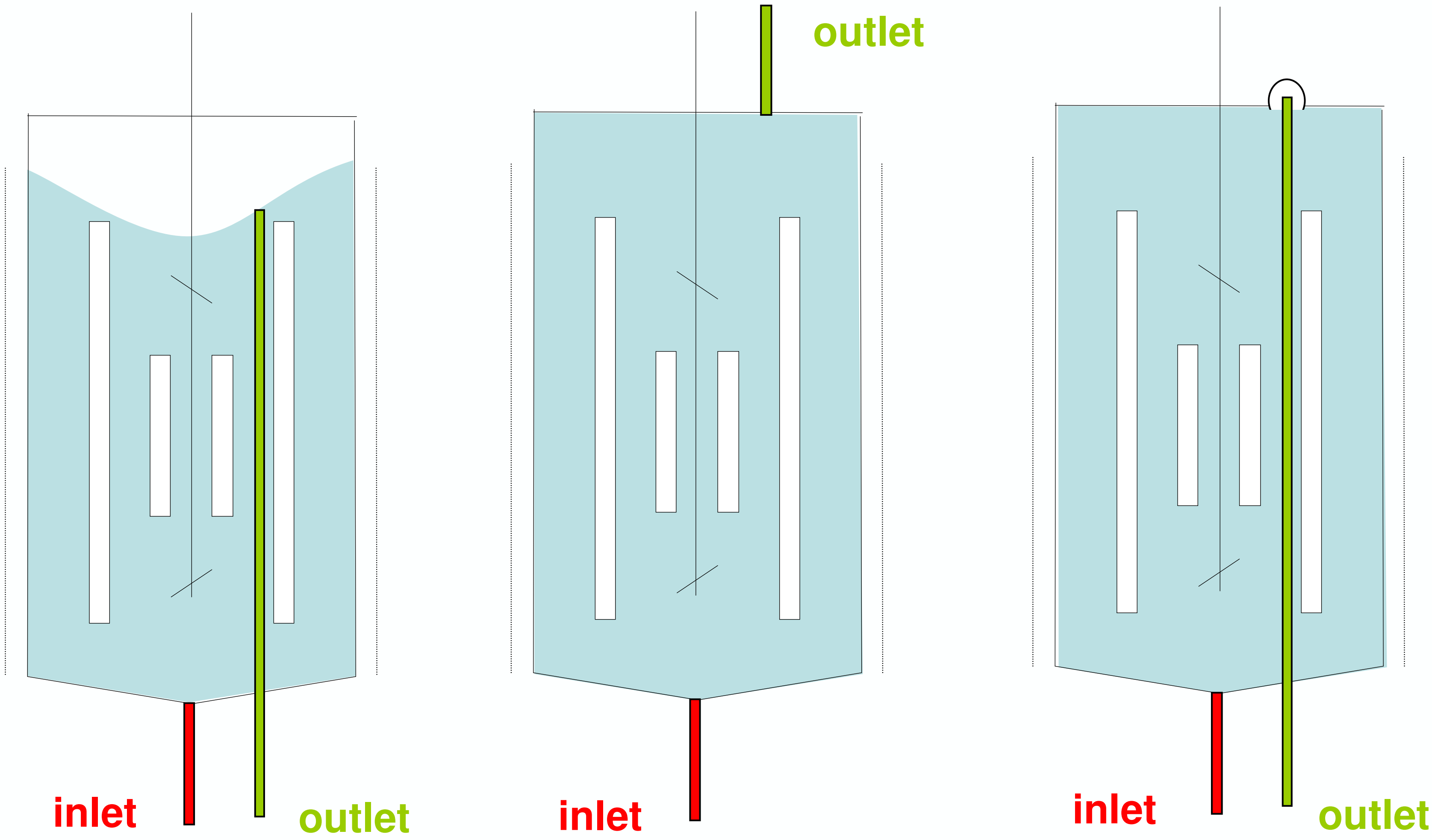
flow pattern



- impeller
  - horizontal central blades
  - top blades tilted by -45°
  - bottom blades tilted by 45°
- flow
  - from centre to wall at middle height
  - from wall to centre at top and bottom
- catalyst location
  - centre of the basket
  - glass wool at top and bottom

outlet configuration

- original
- adaptations

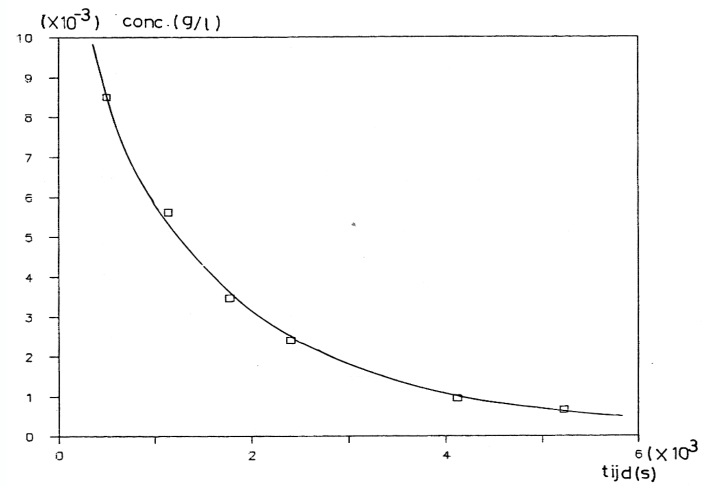


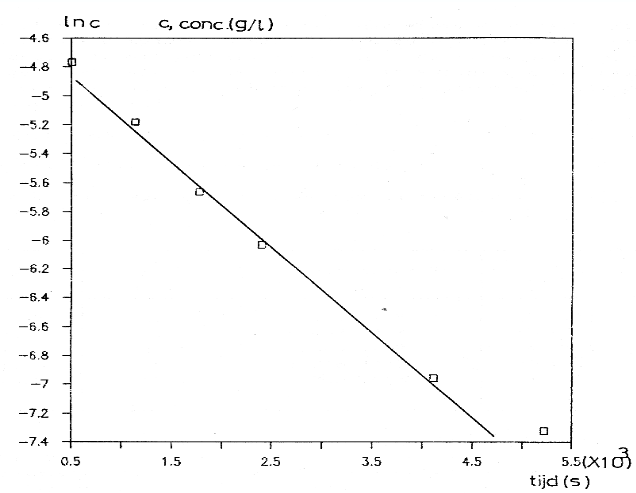
residence time distribution

extended measurements using **water** and **air** with an inlet pulse response of **methylene blue**

Nl_{gas}/l_{liq}	0	200	500
liquid volume (cc)	255	248	200

confirmed by step response of **n-C_{14}** in **n-C_{12}** at reaction conditions





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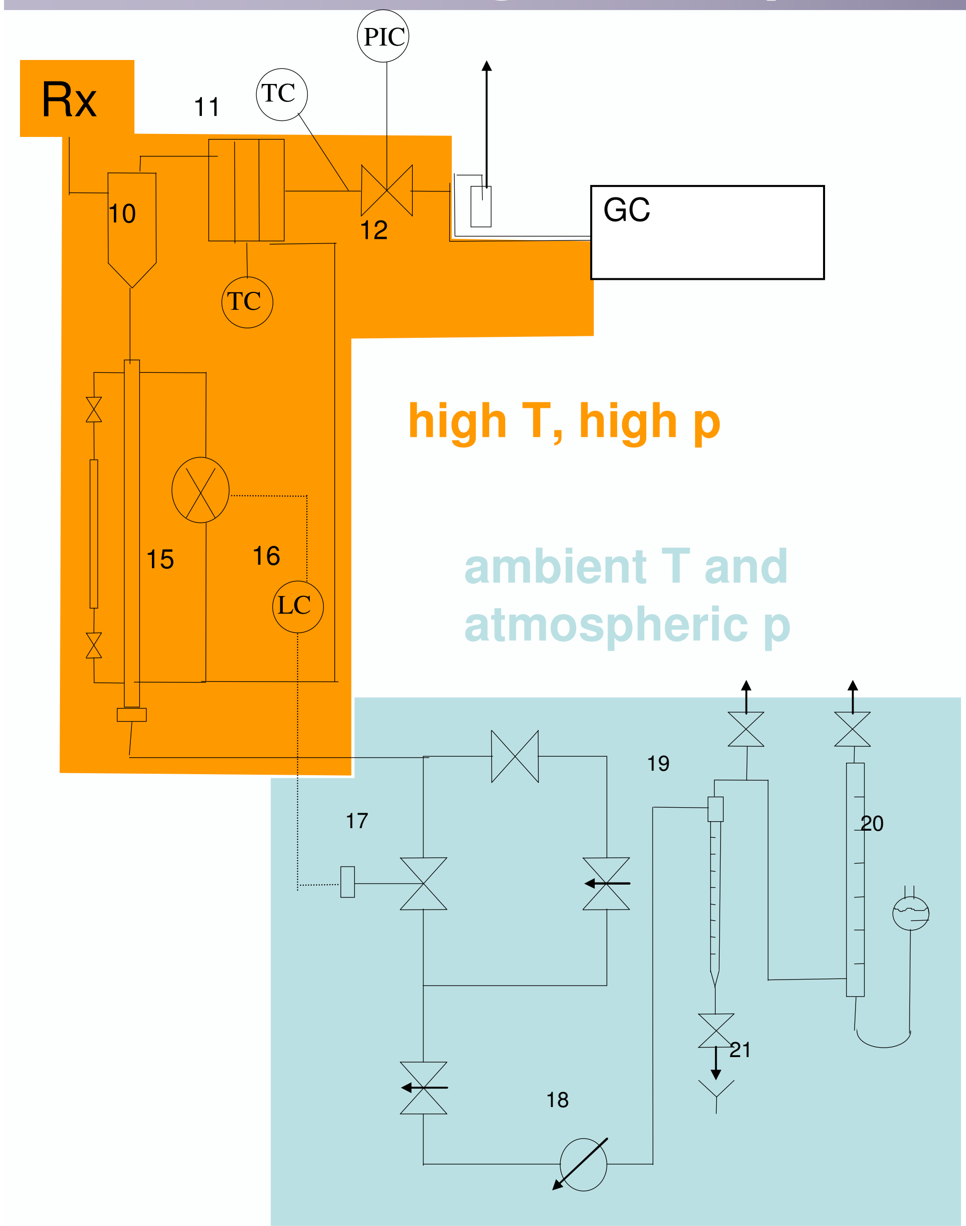
gas liquid separation



separation at reactor conditions (max 250°C)

10 cyclone

11 demister

12 back pressure regulator (gas effluent)

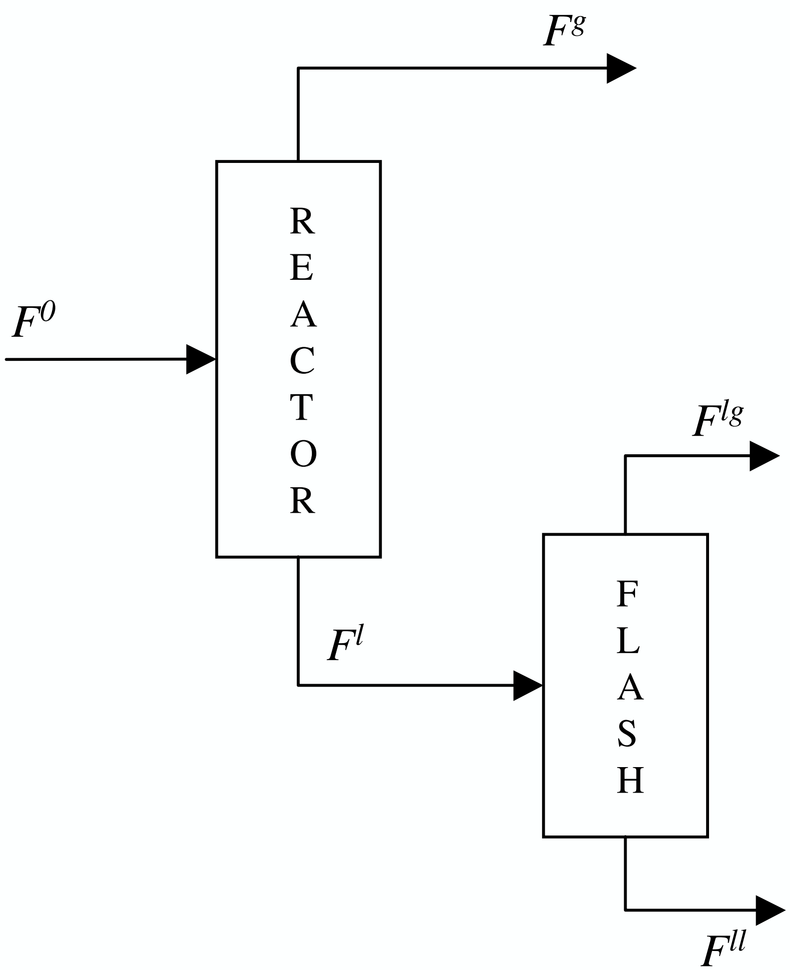
15 level tube

16 level control

17 automated valve (liquid effluent)

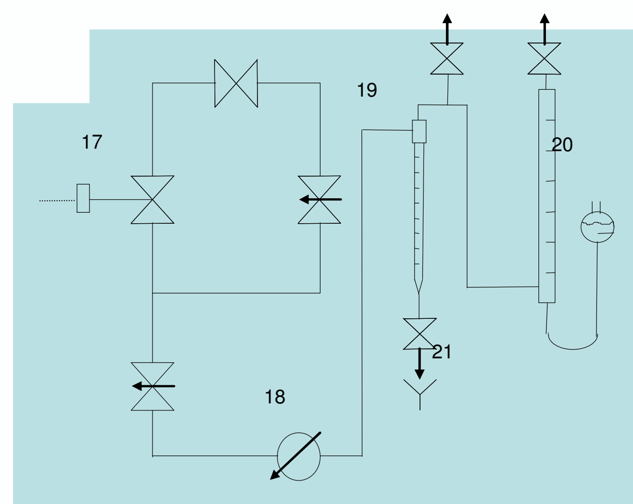
18 needle valve

outlet flow rate measurement



- gas effluent: internal standard
- flashed gas: gas burette
- flashed liquid: liquid burette

amount of internal standard in flashed gas and liquid to be accounted for



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phase equilibrium calculations

set of 2n+2 equations

n → number of components

$$\frac{y_i}{x_i} = K_i = \frac{\Phi_i^l (T, p_t, x_1, \ldots, x_n)}{\Phi_i^g (T, p_t, y_1, \ldots, y_n)}$$

$$F\, z_i = F^l\, x_i + F^g\, y_i$$

$$X = \sum_i x_i - 1 = 0$$

$$Y = \sum_i y_i - 1 = 0$$

fugacity coefficients from equation of state: Peng Robinson, Soave-Redlich-Kwong, with interaction factors for hydrogen according to Moysan (CES 38 1983)

calculation results

- gas and liquid phase composition

$H_2 - nC_{12} -$ benzothiophene (BT)

ratio $nC_{12} - BT$

	exp	calc
gas	34.2	34.0
liquid	28.1	27.5

similar verification for parapur hydrocracking effluent has been performed (Muñoz, 2001)

- gas and liquid fraction in the reactor

	exp	calc
gas	0.2	0.8
liquid	0.8	0.2

calculated values strongly depend on gas – liquid feed ratio

different hold-up for gas and liquid

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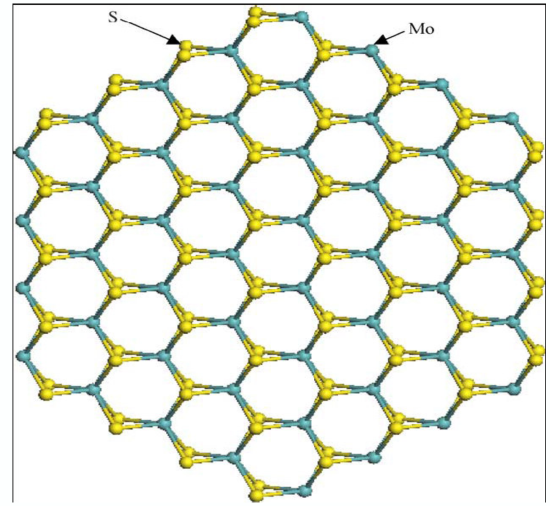
experimental data

catalyst:

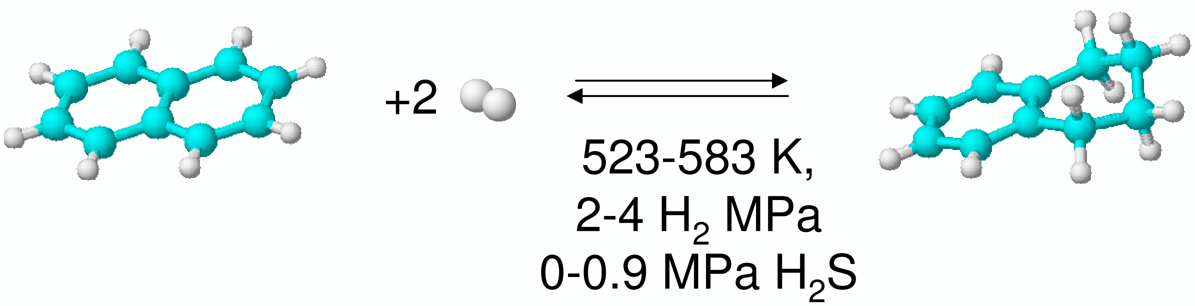


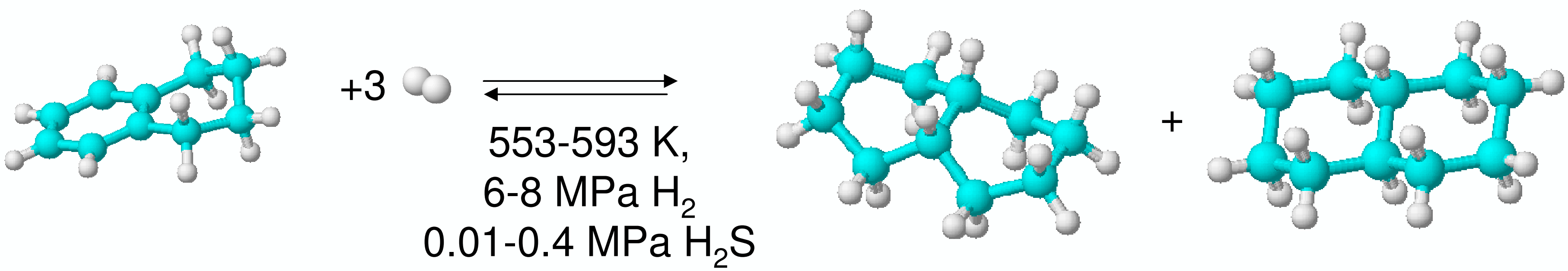
NiMo/γ-Al_2O_3 catalyst Procatalyse EC220/99/23

Mo/Ni = 3.7

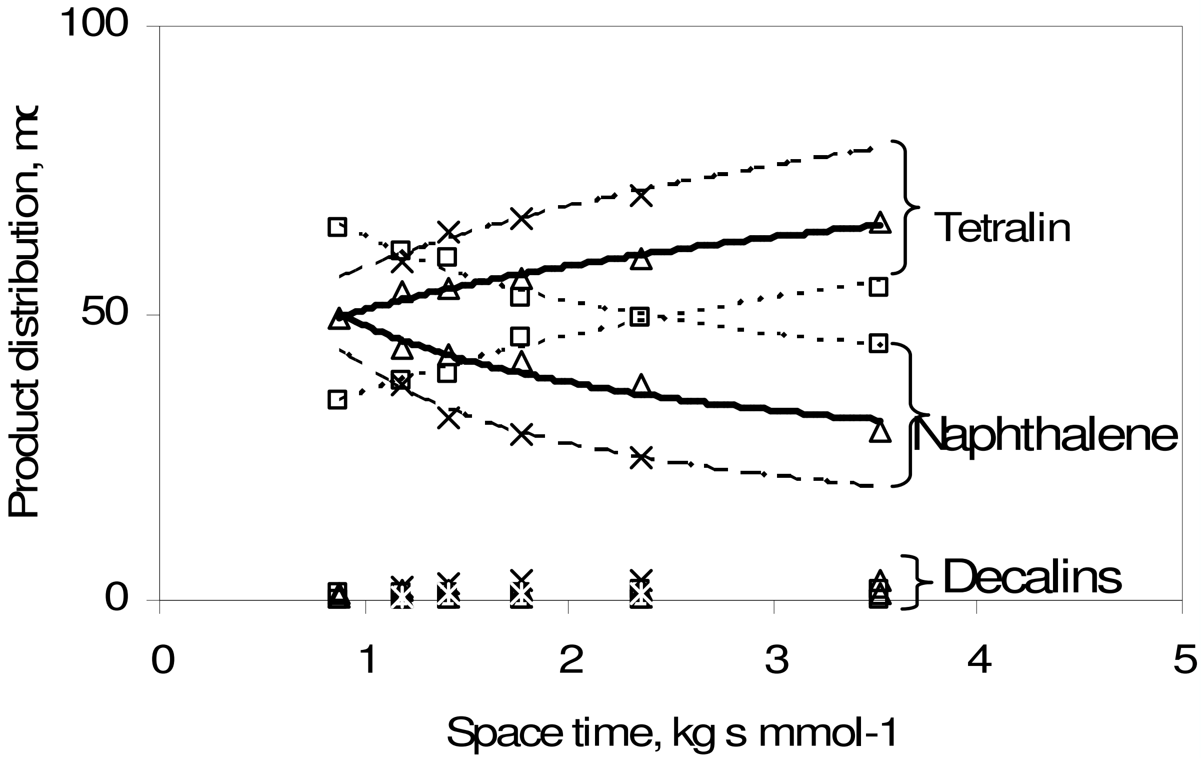
model components and reaction conditions:

parapur solvent (n-paraffin mixture)





experimental results



x 6.0 mol%

Δ 4.5 mol%

□ 2.6 mol%

$S_{N \rightarrow T}$ >94%

553 K, 4 MPa, H_2/H_2S 40,
H_2/Naphthalene 15.5

rate equations

homolytic dissociation

$$R_T = \frac{C_{t,*}^2 k_3 K_{N\rightarrow NH_2} K_N K_{H_2}^{3/2} f_N f_{H_2}^{3/2}\left(1-\frac{f_T}{K_{eq} f_N f_{H_2}^2}\right)}{\left[1+K_N f_N+\sqrt{K_{H_2,*} f_{H_2}}+\frac{K_{H_2S} f_{H_2S}}{\sqrt{K_{H_2,\bullet-S^{2-}} f_{H_2}}}+K_T f_T\right]^2}$$

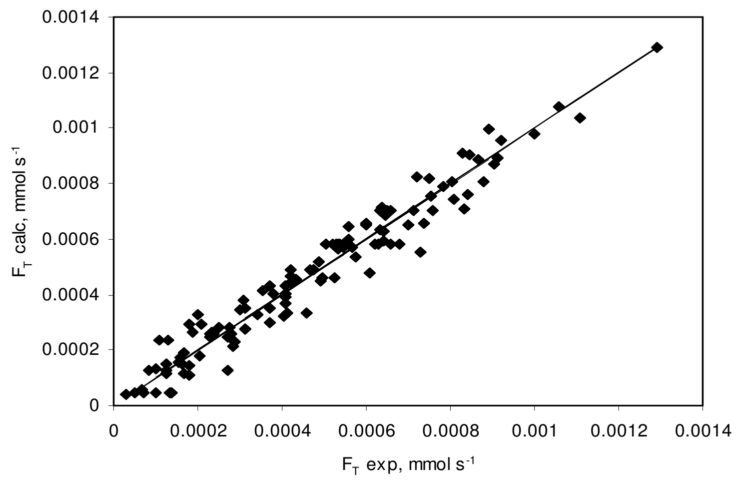
k_3^{comp} ; $K_{H_2,*}$; $K_{H_2,\bullet-S^{2-}}$; K_N ; K_{H_2S} ; K_T

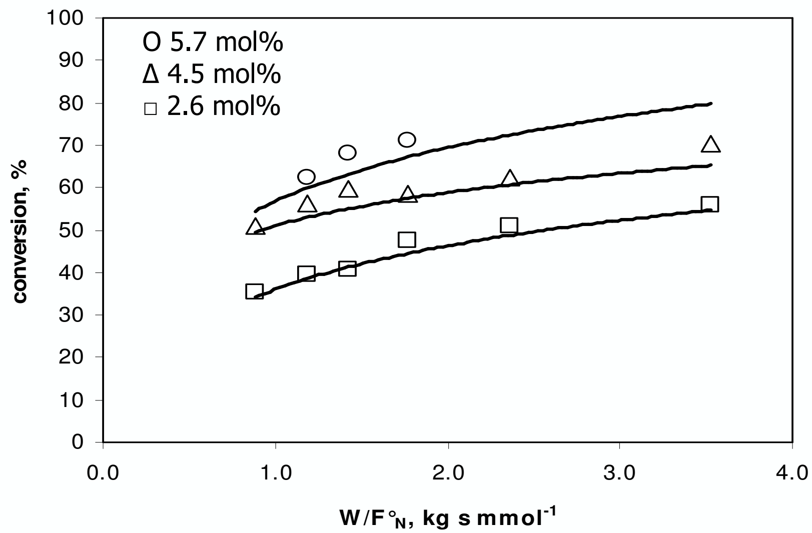
heterolytic dissociation

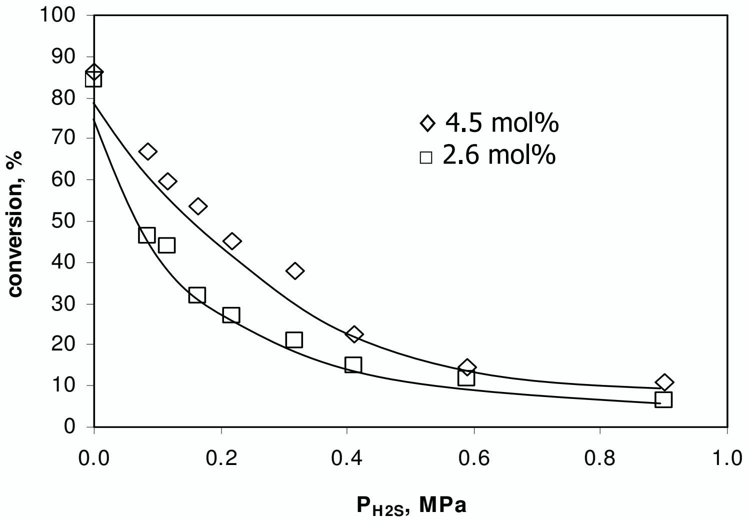
$$R_T = \frac{C_{t,*}^2 k_3 K_{N\rightarrow NH_2} K_N K_{H_2}^2 f_N f_{H_2}^2\left(1-\frac{f_T}{K_{eq} f_N f_{H_2}^2}\right)}{\sqrt{(1+K_N f_N+K_T f_T)(K_{H_2} f_{H_2}+K_{H_2S} f_{H_2S})}\left(\sqrt{1+K_N f_N+K_T f_T}+\sqrt{K_{H_2} f_{H_2}+K_{H_2S} f_{H_2S}}\right)^2}$$

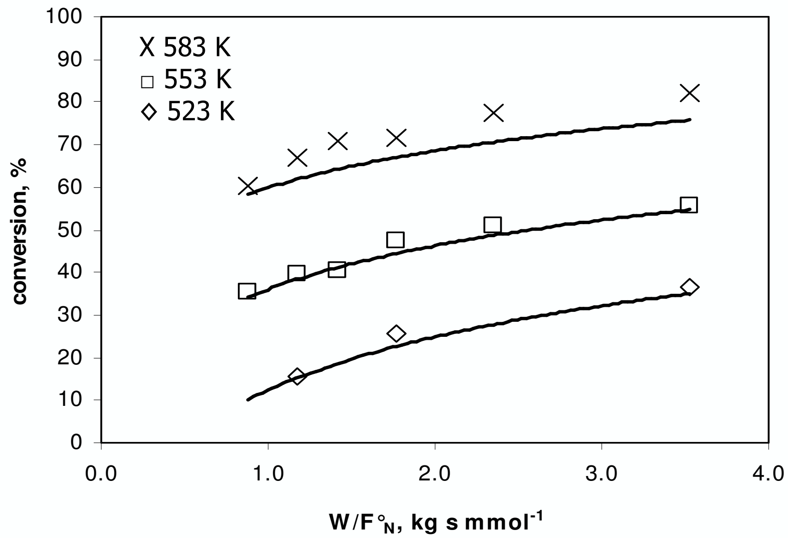
k_3^{comp} ; K_{H_2} ; K_N ; K_{H_2S} ; K_T

model performance









estimated parameter values

Parameter	Model 3	Model 11
E_a^{comp}, kJ mol^{-1}	-41.5 ± 17.5	-37.7 ± 13.2
ΔH^o_N, kJ mol^{-1}	-50.0	-48.0
$\Delta H^o_{H2, *}$, kJ mol^{-1}	-80.0 ± 32.1	-82.5 ± 27.7
$\Delta H^o_{H2, ?\text{-}S^{2-}}$, kJ mol^{-1}	-47.0	n. c.
ΔH^o_{H2S}, kJ mol^{-1}	-128 ± 20.8	-109 ± 19.7
ΔH^o_T, kJ mol^{-1}	-40.0	-40.0

n. c. not considered in the model

Cortes et al. Catal. Today (2008)

conclusions

- pulse and step response measurements are in agreement with an assumed mixed flow behavior of a Robinson-Mahoney reactor
- separation at high T allows assessing phase equilibria
- composition within each phase is found close to equilibrium
- gas and liquid fraction determined by hold-up <> from equilibrium
- Adequate kinetic models can be constructed with physically significant parameters from RM-data