Design of a Mathematic Model for the Calculation of Breakthrough Curves for Desulphurization Units

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1. Introduction

- Hydrocarbons are primary energy carriers and contain sulphur components as a result of their source.
- Within the reforming process sulphur components poison the incorporated catalysts, so the sulphur components must be removed from the hydrocarbons using a desulphurization unit.
- For a detailed design of desulphurization units with adsorbens the knowledge of the adsorption behaviour and a suitable calculation tool is require.

2. Adsorption

- Adsorption is a process in which material accumulates at the interface between two phases.
- These phases can be any of the following combinations: liquid-liquid, liquid-solid, gas-liquid and gas-solid.
- The most efficient equipment for adsorption is the continuous plug flow configuration known as fixed bed.

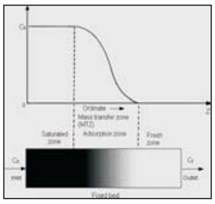


Fig.1 Concentration along fixed bed

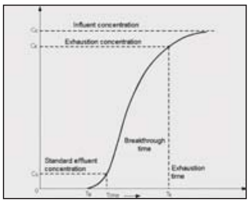


Fig.2 Effluent concentration

3. Theoretical fundamentals for the model

- General assumption: Isothermal gas-solid phase adsorption, radial gradients are neglicted
- General mass balance equation for an infinitesimal element of the fixed bed can be described with a partial differential equation.

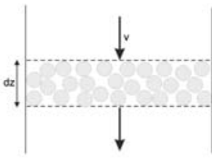


Fig.3 An infinitesimal section of fixed bed

$$-D_L \frac{{}^2 c}{z^2} + \frac{(vc)}{z} + \frac{c}{t} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\bar{q}}{t} = 0$$

Axial dispersion | Variation in gas velocity | Time-depended gas phase concentration variation | Time-depended solid phase loading variation

Further Assumptions / Simplifications

- Constant gas velocity (v=const.)

This assumption can be made because the adsorbate concentration is much smaller than the total gas flow.

$$\frac{(vc)}{z} \quad v\frac{c}{z} \quad c\frac{v}{z} \quad v\frac{c}{z}$$

- Negligible axial dispersion (D_L=0)

The mass balance equation is reduced to:

$$v\frac{c}{z} \quad \frac{c}{t} \quad \left(\frac{1 \quad \varepsilon}{\varepsilon}\right)\frac{\bar{q}}{t} \quad 0$$

- Linear driving force (LDF) model

Used to represent mass transfer in adsorption systems.

$$\frac{\bar{q}}{t} \quad k(q^* \quad q)$$

Solution of differential equation:

$$c \quad \frac{1}{2}c_0[1 \quad erf(\sqrt{\tau} \quad \sqrt{\xi} \quad \frac{1}{8\sqrt{\tau}} \quad \frac{1}{8\sqrt{\xi}})]$$

with $\xi \quad \frac{kKz}{u}\left(\frac{1 \quad \varepsilon}{\varepsilon}\right)$ and $\tau \quad k(t \quad \frac{z}{v})$

Solid Phase Loading Approximation

- Purifier tube is divided into 20 elements averagely.
- All the elements are considered to be homogenous.
- Mass which disappears from the gasflow will be adsorbed by the adsorbent.

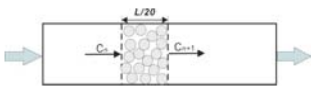


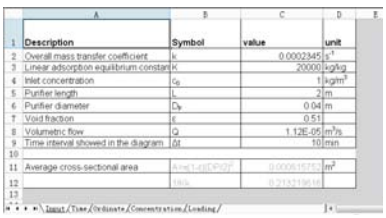
Fig.4 Principle of adsorbent loading calculation

- The mass balance equation for solid phase is:

$$V_a \quad q \quad Q(c_n \quad c_{n\ 1}) \quad t$$

4. Software Development

- After the theoretical investigation, concentrations and loadings versus time and position has been plotted in the programm Microsoft Exel™.
- The model determines the effluent adsorbate concentration and approximate adsorbent loading at different time and position along the purifier tube.



	A	B	C	D
1	Description	Symbol	value	unit
2	Overall mass transfer coefficient	k	0.0002345	s^{-1}
3	Linear adsorption equilibrium constant	K	20000	kg/kg
4	Inlet concentration	c_0	1	kg/m^3
5	Purifier length	L	2	m
6	Purifier diameter	D_P	0.04	m
7	Void fraction	ε	0.51	
8	Volumetric flow	Q	1.12E-05	m^3/s
9	Time interval showed in the diagram	Δt	10	min
10				
11	Average cross-sectional area	[illegible]	[illegible]	m^2
12		[illegible]	[illegible]	
13				

Input / Time / Ordinate / Concentration / Loading

Fig.5 Input sheet

5. Results of parameter variations

- In order to determine which effect a parameter has on the breakthrough curve, a sensitivity analysis by using the calculation tool was carried out.

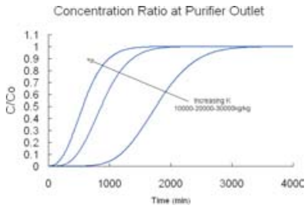


Fig.6 Effect of linear adsorption equilibrium

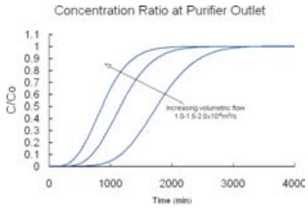


Fig.7 Effect of volumetric flow

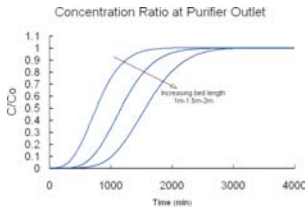


Fig.8 Effect of purifier length

Results for:

- smaller purifier length: the breakthrough curve is steeper
- higher flow rate: the breakthrough time is shorter
- larger linear adsorption equilibrium constant K: the outlet adsorbate concentration increases more rapidly

6. Conclusions and perspectives

- A generalized adsorption system has been studied, with the aim of getting up a mathematical model which can provide a predication of adsorption behaviour on theoretical basis.
- Modelling and simulation of adsorption phenomena have been done under a certain set of simplifying assumptions.
- Although such simple systems are not common in practice, their analysis can provide useful information about the behaviour of more complex systems.
- The tasks of future work are:
  - determination of input parameters
  - measurement of input values from real adsorbent material
  - integration of co-adsorption phenomena if relevant (extensive measurements required)
  - comparison of simulation with realistic desulphurisation behaviour

7. Sulphur analysis

- Precise gas analysis is available which is required to identify traces.
- An extremely sensitive Total-Sulphur-Analyzer (TSA) as well as a gas-chromatograph (GC) with atom-emission-detector (AED) can be utilized for a wide range of experimental investigations.
- With these analysis measurements related to desulphurization or sulphur tolerance of catalysts can be performed.

Fig.9 GC-MSD/AED with Loop Filling Manager

Fig.10 Total-Sulphur-Analyser (TSA)

8. Testing of catalysts and desulphurization materials

- A fundamental requirement for catalyst utilization in reforming and fuel cell technology is the life time.
- The degradation is influenced by the exposure to contaminants like sulphur.
- Degradation mechanism and velocity are known insufficiently.
- In the test facilities of the modern laboratories of ZBT the influence of specific components can be determined.

Fig.11 Desulphurization unit

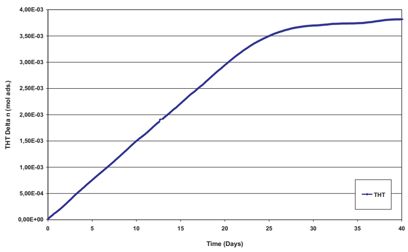


Fig.12 Desulphurization performance of an adsorbens

(10.5 ppm THT in the inlet side)

9. Outlook

- Currently catalysts for the process steps and desulpurization materials are investigated at automated test facilities at ZBT in close co-operation with partners from industry and catalyst suppliers.
- The experimental investigastions are the basis for the evaluation of performance, life time and for designing reactors.

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