SULFUR REMOVAL FROM METHANOL FOR FUEL CELL APPLICATIONS

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Among the different fuel cell types available, the SOFC technology is distinguished among others by fuel flexibility as all: diesel, methane, methanol, syngas, ammonia, bio-methanol, hydrogen and natural gas can be used. Besides hydrogen and methane all other fuels warrant a fuel reformer and cleaning system prior to feeding it to the stack. For SOFCs, particularly a removal of sulfur contamination is crucial as a content of sulfur compounds is strictly limited by their producers to few ppm's or even ppb's.

In this paper a removal of sulfur compounds from methanol is considered, as a presence of them is often detected while methanol is contaminated by diesel or gasoline. Significant amounts of sulfur compounds are also present in methanol when it is obtained as a by-product in pulp production [1].

Purification of methanol by adsorption was here investigated for the following testing system: dibenzothiophene (DBT) – activated carbon (AC), where DBT was taken as a representative of contaminating sulfur compounds. The appropriate model of the adsorption column packed with activated carbon pellets was elaborated and series of simulations carried out.

The analysis of adsorptive purification process was carried out for the system shown in Fig. 1.

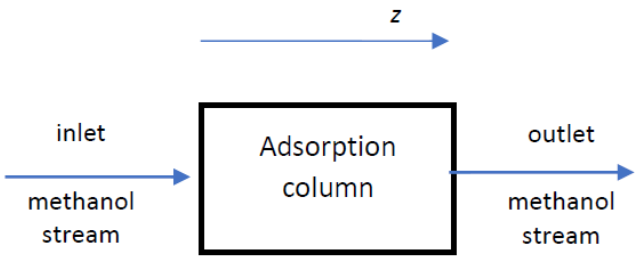

Fig. 1. Schematic diagram of the adsorption column

The following model equation describing the mass balance for DBT in the packed bed was used to determine the concentration profiles along the considered adsorption column at different time moment:

$$\frac{\partial c}{\partial t} = -u\,\frac{\partial c}{\partial z} + D_L\frac{\partial^2 c}{\partial z^2} - \frac{1-\varepsilon}{\varepsilon}\,\rho_s\,\frac{\partial q}{\partial t} \tag{1}$$

where ε – is the bed porosity, u – liquid velocity and ρ_s – density of solid pellets, while c [mol/m^3] and q [mol/kg] are DBT concentrations in liquid and solid phases, respectively. An axial dispersion was also taken into account and the appropriate dispersion coefficient calculated from the following relationship: [2]:

$$D_L = u\,d_s\left(\frac{\varepsilon}{\sqrt{2}\,Re\,Sc} + \frac{1}{2}\right) \tag{2}$$

Adsorption equilibrium was described with the Langmuir equation [2]:

$$q_e = \frac{q_m\,K_L\,c}{1+K_L\,c} \tag{3}$$

while the adsorption kinetics with a pseudo-second order model [2]:

$$\frac{dq}{dt} = k_{2,ad}(q_e - q)^2 \quad (4)$$

The constants (K_L, q_m and $k_{2,ad}$) appearing in equations (3 and 4) was taken from the work [2], then the presented model was implemented in the MATLAB domain and solved with application of the Danckwerts boundary conditions.

Simulation calculations were carried out to find an influence of operating conditions on purification process efficiency. For the process performed at ambient temperature the following inlet and operating conditions were examined: - inlet concentration of DBT in methanol stream, - bed porosity, - liquid velocity in the bed.

An example of the obtained results is shown in Fig. 2, where the DBT concentration in the methanol is shown as a function of time and location along the adsorbent bed.

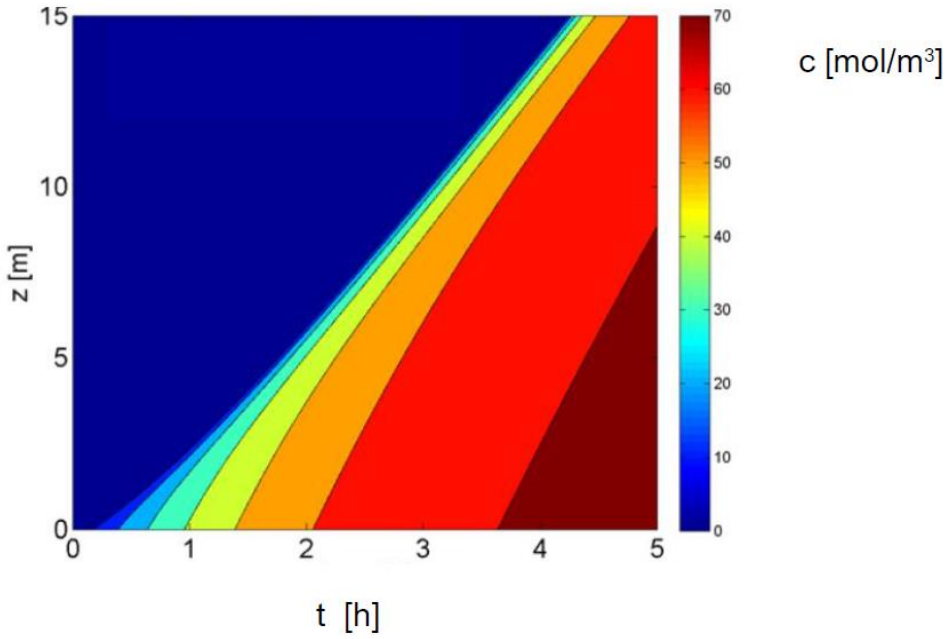

Fig. 2. DBT content in methanol as a function of time and location along the adsorption column

With data presented in Fig. 2 an operating diagram indicating the breakthrough time at chosen column dimensions and operating conditions can be constructed. Then the obtained results can be utilized for effective designing of installation for purification of raw methanol before feeding it to the converter and further to the SOFC.

The investigated adsorptive method of sulfur removal is very promising, however the problem of sorbent regeneration after its saturation with removed sulfur compounds remains still very relevant.

Acknowledgments

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References

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