Simulator for Automotive Evaporative Emissions Restraint Systems

S. Schlüter[*1], T. Hennig[1], E. Schieferstein[1], K. Meller[1]
[1]Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT
*Osterfelder Str. 3, D-46045 Oberhausen, stefan.schlueter@umsicht.fraunhofer.de

Abstract: Fuel vapor restraint systems are used in vehicles to avoid discharge of volatile hydrocarbons from fuel tanks. Until 2020 nearly 10% of all fossil fuels shall be replaced by biofuels upon which bioethanol plays an important role. The topic of this paper is the proper operation of fuel vapor restraint systems depending on the composition of bioethanol-fuel-blends. In laboratory, activated carbons commonly used in fuel restraint systems are tested. Received results and measured data serve as input for a mathematical model realized with COMSOL to simulate the performance of fuel vapor restraint systems depending on bioethanol-fuel-composition.

Keywords: adsorption, activated carbon, biofuels, simulation, vapor restraint system

1. Introduction

Fuel vapor restraint systems are widely used in vehicles to avoid discharge of volatile hydrocarbons from fuel tanks. Until 2020, nearly 10% of all fossil fuels shall be replaced by biofuels upon which bioethanol plays an important role [1]. The topic of this work is the proper operation of fuel vapor restraint systems depending on the composition of bioethanol-fuel-blends. Beyond experimental work on loading activated carbons commonly used in fuel restraint systems, a simulation model for the adsorption/desorption process inside the carbon bed was developed and implemented with COMSOL Multiphysics.

2. Active Carbon Fuel Emissions Simulator (ACES)

Within a funded research project [2] the simulator ACES (Active Carbon Fuel Emissions Simulator) was developed. The model describes a multicomponent gas flow through an adsorber bed with adsorption/desorption mass transfer to/from active carbon under non-isothermal and unsteady conditions (see [2],[3],[4],[5],[6],[7]). Main parts of the model are the conservation laws for mass, species concentrations and heat in the gas phase, the loading of adsorbent with adsorbed species mass, the adsorption isotherms of adsorbed species and the adsorption kinetics.

The mathematical equations are set up with the Mathematics interface and the Chemical Reaction Engineering Module [8] of COMSOL Multiphysics. The time dependent solution of this set of equations is achieved with the fully coupled solution approach and very small initial time steps of about 10^{-6} s.

3. Adsorption model equations

There are some basic assumptions at the start of the modeling work:

- 2-dimensional radial-symmetric adsorber geometry,
- slow laminar flow (Darcy conditions),
- components in the system are ethanol, pentane as gasoline substitute, water and nitrogen as inert component,
- the adsorber is water cooled at the outer surface,
- loading of adsorbent is described by a linear driving force model (LDF model),
- all processes are time dependent.

Under these conditions the set of conservation equations of the developed adsorber model are the impulse conservation, written as Darcy equation,

$$\mathbf{u} = -\frac{1}{150}\frac{\phi^3}{(1-\phi)^2}\frac{d_P^2}{\eta_G}\cdot\nabla P = -\frac{K_D}{\eta_G}\cdot\nabla P$$

the mass conservation for the gas phase,

$$\phi\rho_G\left(\chi_G\frac{\partial P}{\partial t} - \beta_G\frac{\partial T_G}{\partial t} + \sum_{i=1}^{n-1}\varphi_i\frac{\partial c_{i,G}}{\partial t}\right)$$

$$+ \nabla\cdot\left(-\rho_G\frac{K_D}{\eta_G}\nabla P\right) =$$

$$-\rho_S(1-\phi)\sum_i\beta_i^{eff}a_P\left(Y_i^* - Y_i\right)\tilde{M}_i$$

$$\chi_G = \frac{1}{P}\frac{\tilde{M}_{N_2}}{\tilde{M}_G},\ \beta_G = \frac{1}{T_G}\frac{\tilde{M}_{N_2}}{\tilde{M}_G},\ \varphi_i = \frac{1}{\rho_G}\left(\tilde{M}_i - \tilde{M}_{N_2}\right)$$

the component molar conservation for ethanol, gasoline substitute component pentane and water in the gas phase,

$$\phi \frac{\partial c_i}{\partial t} - \nabla \cdot \left(c_i \frac{K_D}{\eta_G} \nabla P \right) - \nabla \cdot \left(\boldsymbol{\delta}_{i,G}^{eff} \nabla c_i \right) =$$
$$-\rho_S \left(1 - \phi \right) \frac{\partial Y_i}{\partial t}$$

the component molar conservation for ethanol, gasoline substitute component pentane and water in the adsorbent phase,

$$\frac{\partial Y_i}{\partial t} = \beta_i^{eff} a_P \left(Y_i^* - Y_i \right)$$

the energy conservation equation for the gas phase,

$$\phi \rho_G c_{P,G} \frac{\partial T_G}{\partial t} + \nabla \cdot \left(-\phi \boldsymbol{\lambda}_{eff}^G \nabla T_G \right) + \rho_G c_{P,G} \mathbf{u} \nabla T_G =$$
$$\phi \frac{\partial P}{\partial t} - \alpha_{GS} a_{GS} \left(T_G - T_S \right)$$

the energy conservation equation for the adsorbent phase,

$$\rho_S \left(1 - \phi \right) \left(c_S + \sum_i Y_i \tilde{M}_i c_{P,i}^{ads} \right) \frac{\partial T_S}{\partial t}$$
$$- \nabla \cdot \left(\left(1 - \phi \right) \boldsymbol{\lambda}_S^{eff} \nabla T_S \right) =$$
$$\rho_S \left(1 - \phi \right) \sum_i \frac{\partial Y_i}{\partial t} \left(\Delta h_i^{ads} + \int_{T_S}^{T_G} c_{P,i}^G \, dT \right) \tilde{M}_i$$
$$+ \alpha_{GS} a_{GS} \left(T_G - T_S \right)$$

and the energy conservation equation for the solid adsorber wall,

$$\rho_W c_W \frac{\partial T_W}{\partial t} + \nabla \cdot \left(-\lambda_W \nabla T_W \right) = 0$$

For the implementation in COMSOL Multiphysics the component equations in the gas phase are implemented with the *Diluted Species in Porous Media* branch of the Reaction Engineering module and the energy equations are implemented with the *Heat Transfer in Porous Media* branch of the Heat Transfer module. This was done to use the consistent stabilization possibilities of COMSOL Multiphysics available with these modules. The other equations given above are implemented equation based with suitable parts of the Mathematics module.

The initial and boundary conditions to solve these equations are given experimental inlet conditions (flow and concentrations) at the adsorber inlet and a given outlet pressure of 1 atm. At the outer surface the adsorber wall is water cooled with an appropriate heat transfer coefficient calculated with an empirical equation. Initially, the system is at cooling water temperature and filled with pure nitrogen.

These equations are implemented with *COMSOL Multiphysics* in a 2-d axisymmetric model. Created *meshes* are based on mapped structures. *Discretization* is set to default conditions in all interfaces. The time dependent solver is set up in fully coupled mode with the *Pardiso* direct linear solver and *Jacobian Update* on every iteration. Time stepping options depend on the solution scenario, but in most cases an initial step of 10^{-6} s and a maximum step of 10 s are appropriate values. The simulation times are in the range of 20 to 30 min on a high end PC.

It should be noted, that in addition to these basic conservation equations a large overhead of specific equations is necessary for the definition of specific adsorption physics. These equations apply for

- adsorption isotherms of the components
- heat and mass transfer coefficients
- molar diffusion and heat conduction coefficients

These equations were clearly arranged in variable blocks and analytic functions, so the COMSOL model stays comprehensible and clearly documented for further work.

In laboratory experiments, the adsorption physics of the ethanol/gasoline/active carbon system were studied (see [2]). Exemplary, in **Fig. 1** the experimental apparatus for studying break through curves is shown.
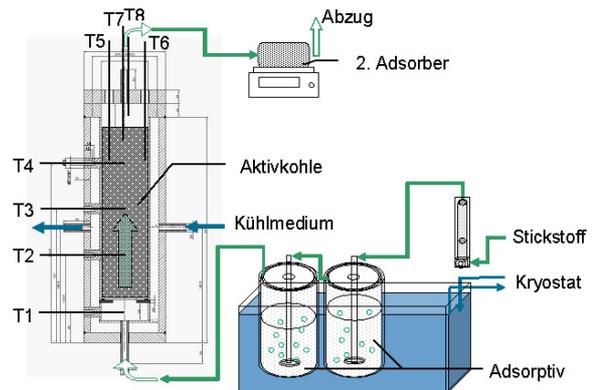

Figure 1. Experimental installation for the study of break through experiments with fuel gases and active carbon

In the scope presented here these important additional topics cannot be described in detail and are subject of further papers [2].

4. Simulation cases and results

The simulation was set up for the loading of a moisturized active carbon bed in a cylindrical adsorber with a gas mixture of pentane, ethanol, water and nitrogen. Pentane is used here as a reference gas instead of gasoline with standard specifications. Experiments presented here are performed up to the total loading of the active carbon beds with pentane [2], which is detected by the break-through of pentane at the adsorber outlet with a second weighted "police adsorber". The simulations were run under the same physical conditions as in the experiments, and the thermodynamic conditions inside the bed are recorded over time.

Fig. 2 and **Fig. 3** shows the temperature and the molar fraction of pentane in the gas phase after 32 min from process start.
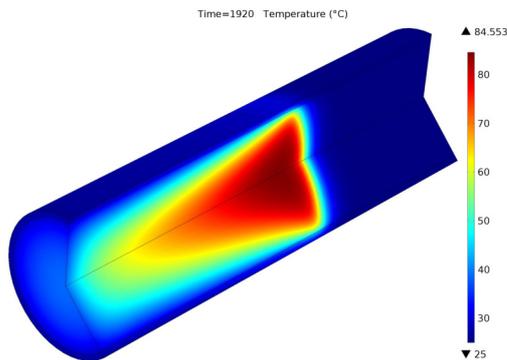
The simulation shows that there is a small mass transfer zone at the loading front with large gradients in many thermodynamic quantities. Due to adsorption heat, the temperature increases up to 130°C depending on adsorption conditions. The process shown here produces a damped temperature increase to nearly 90°C because of loading a *moisturized* active carbon at initial conditions. Moisturized active carbon shows smaller capacities for hydrocarbons which is considered in the model. Molar fractions of pentane and ethanol in the gas phase nearly become Zero close behind the adsorption front. Thus, the adsorber works in a very efficient mode.

In **Fig. 4** and **Fig 5** the loading of pentane and ethanol on the active carbon after 32 min from process start (same time as before) is shown. The loading equilibria for the gas components are strongly temperature dependent, which results in a strong multiphysics coupling between energy and mass transfer. So, the loading fields in the adsorbent are reflecting the temperature field in the geometry.
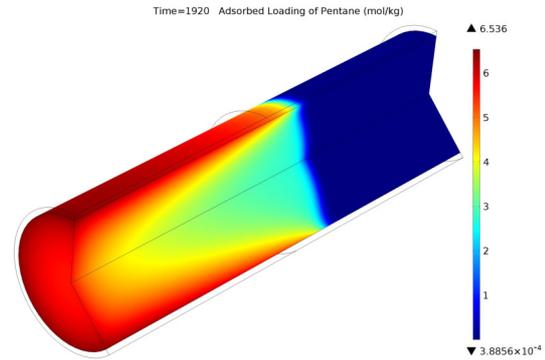

Time=1920   Temperature (°C)

Figure 2. Temperature field inside the active carbon bed at t = 32 min after process start

Time=1920   Adsorbed Loading of Pentane (mol/kg)

Figure 4. Pentane adsorbent loading field inside the active carbon bed at t = 32 min after process start

Time=1920   Molar Fraction of Pentane (1)

Figure 3. Pentane molar fraction field inside the active carbon bed at t = 32 min after process start

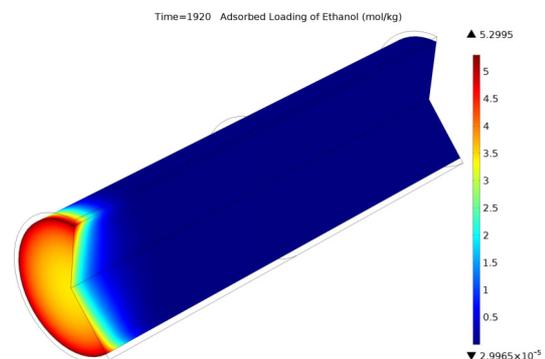Time=1920   Adsorbed Loading of Ethanol (mol/kg)

Figure 5. Ethanol adsorbent loading field inside the active carbon bed at t = 32 min after process start

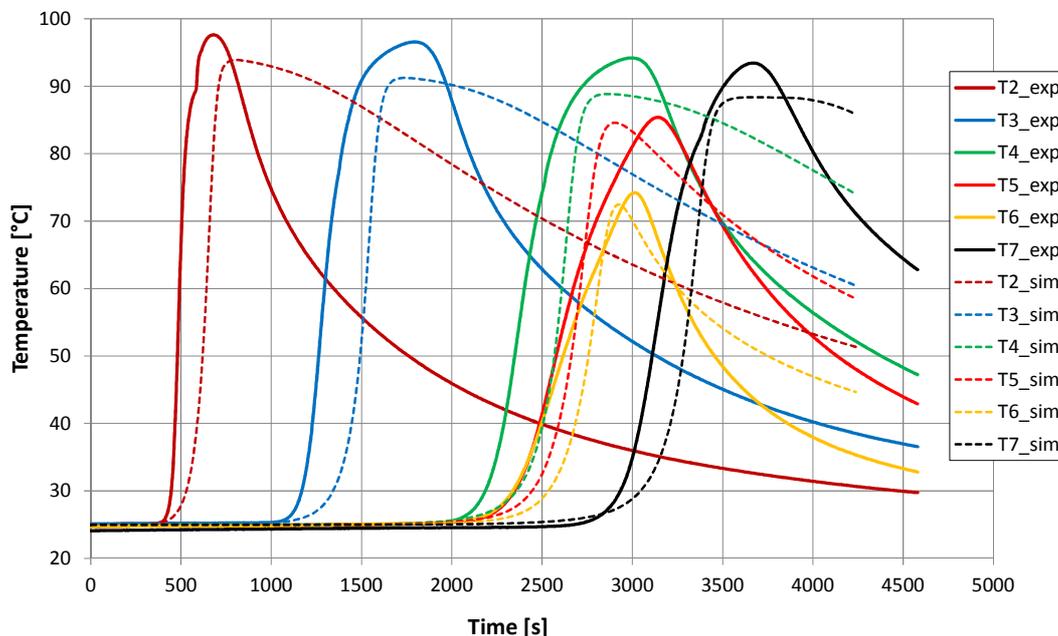**Mixture 78% Pentane / 22% Ethanol on wetted Active Carbon (1), 20 l/h N$_2$**

Figure 6. Temperature point measurements inside the adsorber – experimental findings and simulation

In the experiments temperature probes are installed at certain points inside the bed. In COMSOL simulations these probes are directly reflected with the point probe facility. In **Fig. 6** an example is given of measured and simulated temperature probes for an experiment (not the same as for Figs. 2 to 5). It can be seen that

1. the time of temperature increase,
2. the time rate of temperature increase and
3. the maximum temperature of each probe

are reproduced well within the simulation.

In **Figs. 7** and **8** the results of the simulation of an adsorption/desorption cycle are shown. Desorption was done with air at 20°C directly after an adsorption phase; the air inlet was on the top of the adsorber (countercurrent to adsorptive flow). From the results it can be seen, that the maximum adsorption temperatures in the bed become lower from cycle to cycle. The reason is the imperfect regeneration of the adsorber during desorption – a part of the adsorbed gas remains at the lower part of the adsorber and in the following adsorption phase the capacity here is lowered, which results in a lower temperature increase. This effect is intensified from cycle to cycle and is strongly depending on the implemented desorption kinetics of the process.
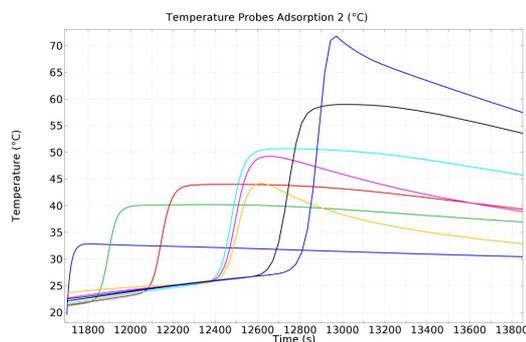

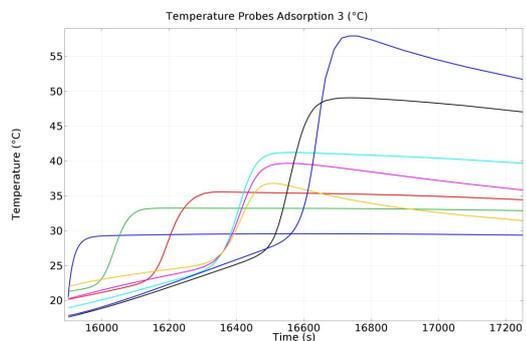**Figure 7**. Temperature development inside the active carbon bed, second adsorption cycle

Figure 8. Temperature development inside the active carbon bed, third adsorption cycle

5. Conclusions

Dynamic modeling is a powerful tool to understand fuel vapor restraint systems used in the automotive sector. Temperature, gas concentration and adsorptive loading fields are coupled closely together in such systems and the multiphysics coupling qualities of COMSOL are very practical to model and simulate the process. Temperature point measurements show the high quality of the model, and with the 2d-field results we can look somewhat deeper inside the adsorbent bed, which will result in a better understanding of the adsorption process.

The ACES simulator is an experimental proved simulation tool for the loading of active carbon canisters with fuel gases. In actual research the model will be used to simulate periodical adsorption and desorption in automotive driving circles.

6. References

1. Richtlinie 2003/30/EG des Europäischen Parlaments und des Rates der Europäischen Union vom 8. Mai 2003 zur Förderung der Verwendung von Biokraftstoffen oder anderen erneuerbaren Kraftstoffen im Verkehrssektor. Amtsblatt der Europäischen Union, L 123/42-L123/46, 17.5.2003

2. Schieferstein, E., Schlüter, S., Hennig, T., Meller, K., Lange, M., Möller, A.: Untersuchung von Kraftstoffdampf-Rückhaltesystemen bei Einsatz von Ethanol-haltigen Biokraftstoffen, Chemie-Ingenieur-Technik **86** (6) 2013, 934-943

3. G. A. Lavoie, P. J. Johnson, J. F. Hood, Carbon canister modelling for evaporative emissions: adsorption and thermal effects, International Spring Fuels & Lubricants Meeting, **961210**, 1996, 1-22

4. P.J. Lavoie, J. R. Johnson, J. R. Jamrock, Activated carbon canister performance during diurnal cycles: An experimental and modeling evaluation, in: SAE Technical Papers Series, **971651**, 1997, 253-263

5. P.J. Lavoie, Y. A. Imai, J. R. Johnson, A fuel vapour model (FVSMOD) for evaporative emissions systems design and analysis, in: SAE Technical Papers Series, **982644**, 1998

6. B. Sankararao, S. K. Gupta., Modeling and simulation of fixed bed adsorbers for multi-component gaseous separations, Computers and Chemical Engineering **31**, 2007, 1282-1295

7. W. Kast, Adsorption aus der Gasphase, VCH-Verlag, Weinheim, 1988

8. Chemical Reaction Engineering Module User's Guide, Version 5.2a, COMSOL AB, 2016

7. Acknowledgements

8. Nomenclature

a	volumetric interface area, m^2/m^3
c_i	molar concentration, mol/m^3
c_p	specific heat capacity, $J/(kg \cdot K)$
d	diameter
Δh	heat of adsorption, J/kg
K_D	Darcy permeability, m^2
$\tilde{M}$	molar mass, kg/mol
P	pressure, Pa
q	volumetric heat source, W/m^3
t	time
T	temperature, K
u	Darcy velocity, m/s
y	molar fraction, mol/mol
Y	molar loading per mass of adsorbent, mol/kg
Y^*	equilibrium loading, mol/kg
α	heat transfer coefficient
β	volumetric expansivity, $1/K$
β^{eff}	mass transfer coefficient, m/s
χ	isothermal compressibility, $1/Pa$
δ	diffusion coefficient, m^2/s
ϕ	porosity, m^3/m^3
φ	compositional derivative coefficient, 1
η	dynamic viscosity, $Pa \cdot s$
λ	heat conductivity, $W/(m \cdot K)$
ρ	specific density, kg/m^3

Indices

*	in phase equilibrium
ads	adsorption
eff	effective
G	gas phase
i	component i
j	phase j
n	inert gas component n
P	Particle
S	solid phase
W	wall