Adsorbed Renewable Energy Gas Storage

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Abstract— **Gases like hydrogen and gas mixtures like biogas are an important renewable energy resource. For storing, the gas is compressed and transferred to pressure vessels A sustainable and effective alternative is the adsorption of the gas by porous media. Adsorbed gas storage is of particular relevance for vehicles, where the fuel storage volume is limited. The storage performance of activated carbon beds for methane, carbon dioxide, hydrogen and the binary mixtures with methane is investigated. A lumped parameter model is used to describe composition, pressure, mean temperature and flow rate. The Dubinin-Astakhov isotherm is used to describe the adsorbed amount at different temperatures and pressures. The resulting set of transient differential equations is solved numerically. The charging process with regard to filling time and temperature is examined. The discharge process with regard to discharge rate, concentration and temperature is investigated. The charge and discharge time are significantly influenced by the heat of adsorption. For the outlet flow the composition of the gas mixture changes over time.**

Keywords—adsorption, gas storage, activated carbon, methane, hydrogen carbon dioxide, mixtures, mobility

I. INTRODUCTION

A carbon neutral alternative to fossil fuels are green fuels or biofuels. Gaseous green fuels are mostly based on methane or hydrogen resulting from many different production processes. Electrical energy from wind or solar power can be transformed and stored in chemical form as hydrogen or hydrocarbons. The resulting hydrogen may be used to enrich methane. Biogas is a mixture of several gases with the main components methane and carbon dioxide. The conditioning to pure methane is expensive, partially conditioned biogas contains significant levels of carbon dioxide.

The use of such gas mixtures as fuels is investigated with regard to combustion and operation of furnaces and engines [1, 2]. In addition, also the questions referring to the storage of these gas mixtures should be addressed.

Gases are generally stored in high pressure vessels. A recent alternative is adsorption storage in activated carbons (AC) or metal organic frameworks (MOF) [3-7]. Thus the volumetric capacity is increased. Due to the heat of adsorption special care has to be taken with regard to the heat management and with regard to the charge and discharge rate.

Adsorption gas storage is of particular interest for use as fuel tanks in vehicles. Thus some experience is already available concerning the storage of methane (natural gas) and hydrogen (for fuel-cells) [6-7]. For the investigation lumped parameter models and CFD models are used. As the CFD analysis show [8-10], for simple geometries and cooling by natural convection only, the temperature and pressure distribution is roughly uniform. Thus a lumped parameter model might give a feasible estimate at reduced computational cost [10].

With regard to the storage of gas mixtures there is less data available. Most data is concerned with the investigation and modelling of adsorption equilibria in various media or with the purification of one component (i.e. methane) [11-13].

In this work the feasibility of adsorption storage for biogas and enriched methane is investigated. Therefor the charging and discharging of a representative adsorption tank is investigated theoretically.

As representative fuels methane, a binary mixture of methane and 20% carbon dioxide (biogas) and a binary mixture of methane and 20% hydrogen (enriched methane) are considered.

The analysis is performed for a 33 litre cylindrical gas tank, height 1.19 m and diameter 0.229 m with activated carbon as adsorbent. The heat transfer is by natural convection to the ambient.

The governing equations are set up and solved numerically using a GNU Octave script. As a result of these simulations the influence of charging time and pressure levels are presented.

During charging the temperature and concentration in the adsorbed phase and gas phase are computed. The concentration variations of the outflowing gas mixtures are shown.

II. METHODOLOGY

A lumped parameter model for the cylindrical adsorption tank with area averaged pressure and temperature values is derived based on the mass and energy balance equations and an adsorption isotherm model.

Mass balance of gas in the tank, gas and adsorbed phase

$$\frac{dm}{dt} = V_b \varepsilon \; \frac{d\rho}{dt} + V_b \rho_b \frac{dq}{dt} \qquad (1)$$

Volume of adsorbent V_b, total porosity ε and amount of gas adsorbed q. The gas density is computed with the ideal gas equation of state $\rho = P\,M\,/\,R\,T$.

The inflow and outflow (mass flow rate) are prescribed. Charging is implemented by a positive mass flux and an increase in pressure, discharging by a negative mass flux and decreasing pressure.

Charging is modelled by a constant mass flux, starting with ambient pressure (100 kPa) and temperature (300 K) until the maximum pressure is reached. Discharging is modelled by a constant mass flux, starting with maximum pressure and ambient temperature (300 K) until the ambient pressure (100 kPa) is reached.

Energy balance

$$C_{eff}\frac{\partial T}{\partial t} = h \cdot (T - T_{ambient}) \cdot A + \rho_b H \frac{\partial q}{\partial t} \qquad (2)$$

Area averaged temperature T, effective heat capacity C_{eff} (J/ kg K), the heat transfer coefficient $h = 5$ W/m^2 for natural convection, the exterior surface A of the cylindrical tank, the average heat transfer coefficient, the packing density ρ_b and the heat of adsorption H and amount adsorbed q of the gas or gas mixture.

The gas phase and the adsorbed phase are assumed to be in equilibrium.

Dubinin-Astakhov equation for the adsorption isotherm

$$q_i = \rho_{ads} W_o \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] \qquad (3)$$

The adsorbed gas density $\rho_{ads} = \rho_{boil}\,/\,\exp(\alpha\,(T\text{-}T_{boil})\,)$ is computed with the temperature T_{boil} and liquid density ρ_{boil} at boiling point and the thermal expansion of liquefied gases $\underline{\alpha}$=2.5 10^{-3} 1/K.

The adsorption potential $A = R\,T\,\ln(P_s/P)$ is determined with the saturated vapor pressure calculated from the critical values $P_s = P_{cr}\,(T/T_{cr})^2$.

The total volume adsorbed is computed from the pure vapor adsorption volumes assuming volume proportionality, $q_t = z_1\,q_1 + z_2\,q_2$. Based on the volume fractions z_i. The reference amount q_i for each component is calculated at the total pressure. The binary gas mixtures considered consist of 20% mole fraction methane and 20% mole fraction carbon dioxide and hydrogen respectively.

The data for the adsorbent (Norit RGM1), micropore volume of the adsorbent $W_0 = 3.3$ 10^{-4} m3/kg and reference adsorption energy $E_0 = 25.04$ kJ/mol are taken form the literature [10], as well as the data for the adsorbed gases (methane $\beta = 0.35$ and $n = 1.8$, carbon dioxide $\beta = 0.36$ and $n = 1.8$, hydrogen β=0.22 n=2) [11-13]. The property values are computed with data from [14].

The differential equations are discretized with a Euler-forward scheme. The time steps are adjusted to ensure a steady change in the area-averaged pressure. The step size is chosen to ensure the independence of the numerical solution

from the step size (average deviation smaller 1%). The adsorption equilibrium is solved every time step by iteration. In order to facilitate the convergence and the computational effort constant property values are used.
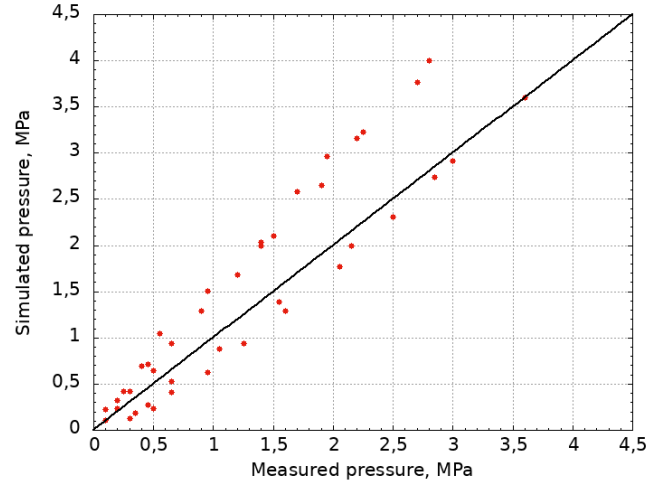

Fig. 1. Comparison of computed and measured pressure values for the charging and discharging of a small cylindrical tank with different flow rates.
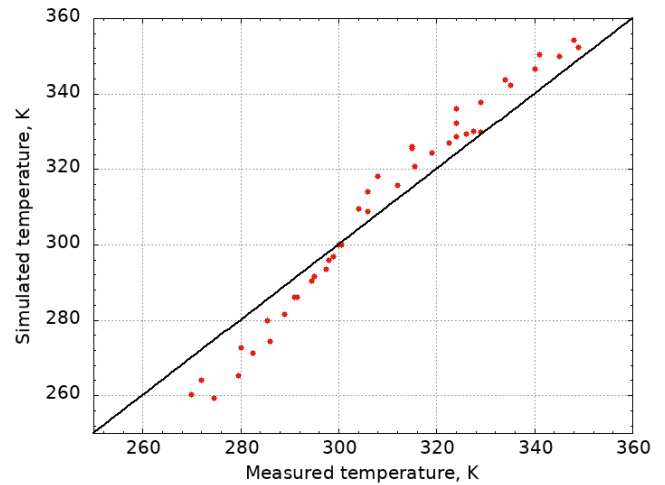

Fig. 2. Comparison of computed and measured temperature values(centre bed temperature) for the charging and discharging of a small cylindrical tank with different flow rates.

The results of this model are compared with measured data for methane from the literature. Computed and measured pressure and temperature data for the charging and discharging of a small cylindrical tank are shown in Fig. 1 and Fig 2. The deviations are bigger for high flow rates when the temperature distribution is more uneven. The quality of the simulated result may be improved by considering variable fluid properties. Nevertheless a qualitative assessment of the main phenomena using this simulation model is possible.

III. Results

A. Charging and Discharging of Pure Methane

For the charging and discharging of the 33 litre tank with pure methane the pressures, the temperatures and the

distribution of the adsorbed phase and the gas phase for different flow rates is investigated.

As the methane enters the tank the pressure rises and due to the heat of adsorption there is also a rise in temperature. Increasing the incoming mass flow rate, increases the heat generated in the tank. A part of this heat is discharged to the ambient by natural convection.
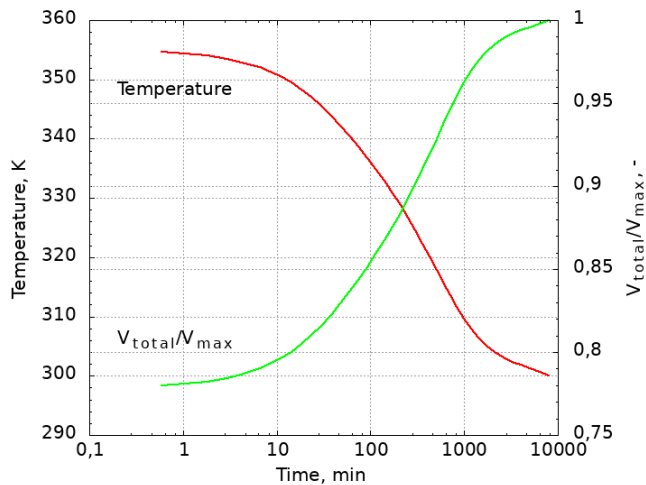

Fig. 3. Charging of a 33 litre adsorption tank with methane. Temperature and storage efficiency for different charging times.
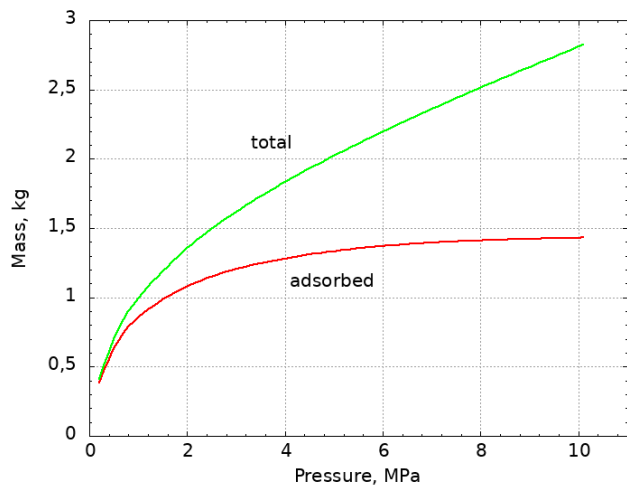

Fig. 4. Charging of a 33 litre adsorption tank with methane. Total mass of methane stored and mass of methane adsorbed for different pressure levels.

With an increase in temperature the amount of gas that can be adsorbed decreases, thus reducing the storage capacity of the adsorption tank, Fig 3. With increasing flow rates (decreasing charging times) there is a limit where the heat generated cannot be dissipated anymore. Enhancing the heat transfer (i.e. forced convection, increasing the surface) can shift this limit to smaller charging times. With decreasing flow rate (increasing charging time) the generated heat is transported to the ambient and the full capacity of the adsorption tank can be used. Further decreasing the flow rate has no significant advantage.

With increasing pressure the amount of gas stored in the tank increases, in the adsorbed phase as well as in the gas phase, Fig. 4. The amount of the species that is adsorbed is

significantly higher for smaller pressures as the influence of the pressure on the gas phase (compression) is more distinct. Thus the adsorption gas storage is more advantageous for smaller pressure levels.

B. Charging and Discharging of Methane Mixtures

Based on the results for pure methane a constant mass flow rate of 0.31 g/s and a maximum pressure of 3.6 MPa is chosen. The order of magnitude for charging and discharging is one hour. (This flow relates to the energy needed to accelerate a car in 10s to 100 km/h using methane as a fuel. For a comparable energy the flow rate of the methane - hydrogen mixture is slightly smaller and for the methane – carbon dioxide mixture the mass flux has to be doubled.)

The additional components have a distinct but not a considerable influence on the performance of the adsorption tank. Charging and discharging times as well as the maximum temperature are comparable, Fig. 5-11. During the charging and discharging the concentrations of methane in the gas phase and in the adsorbed phase are changing.

For the methane-carbon dioxide mixture the times needed for charging and discharging as well as the heat generated are similar to pure methane. At low pressures the amount of carbon-dioxide adsorbed is significantly higher then the amount of methane. With discharging the fraction of methane is higher in the outflowing gas mixture then in the inflowing mixture. During the discharging the methane concentration slightly decrease. At the end of the discharging process there is still an additional amount of carbon dioxide in the tank, as not all of the charged carbon dioxide is discharged. Using partially upgraded biogas as a fuel requires additional storage capacity (for the carbon dioxide with no energetic value). The changes in the composition of the outflowing gas mixture should pose no problem for many technical applications. The carbon dioxide in the tank might accumulate requiring some sort of regeneration.

For the methane–hydrogen mixture the maximum temperature is slightly bigger as the charging time is somewhat smaller and the heat of adsorption for hydrogen is bigger. At the beginning of the charging (low pressures) the amount of methane in the gas phase is considerably higher then in the adsorbed phase, at the end of the charging process the levels are comparable. With discharging at the beginning the hydrogen concentration is big and at the end the hydrogen concentration is significantly smaller. This leads to varying levels of energy with a constant mass flux. Using upgraded methane in adsorption tanks might require additional control and instrumentation in order to take into account the variation of the energy content.
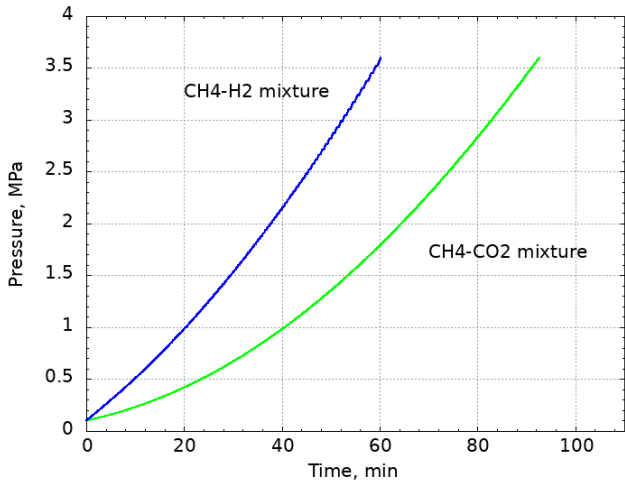
Fig. 5. Charging of a 33 litre adsorption tank with methane and methane mixtures, pressure over charging time
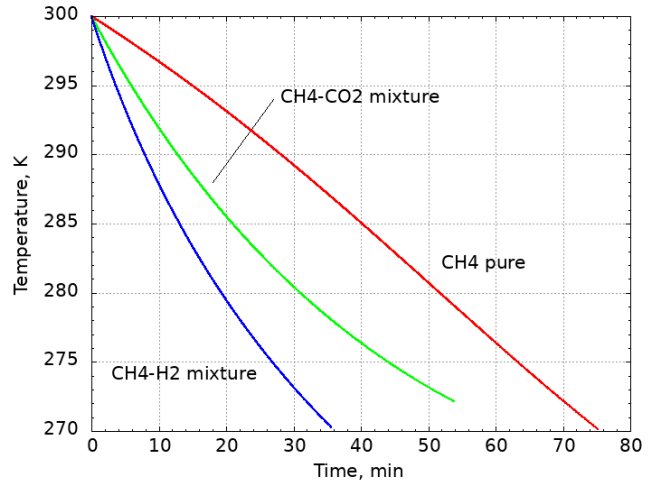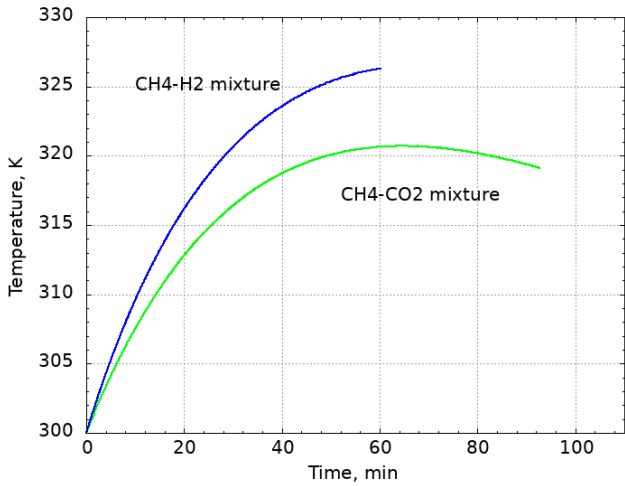

Fig. 6. Charging of a 33 litre adsorption tank with methane and methane mixtures, temperature over charging time.

Fig. 7. Discharging of a 33 litre adsorption tank with methane and methane mixtures, pressure over discharging time

Fig. 8. Discharging of a 33 litre adsorption tank with methane and methane mixtures, temperature over discharging time.

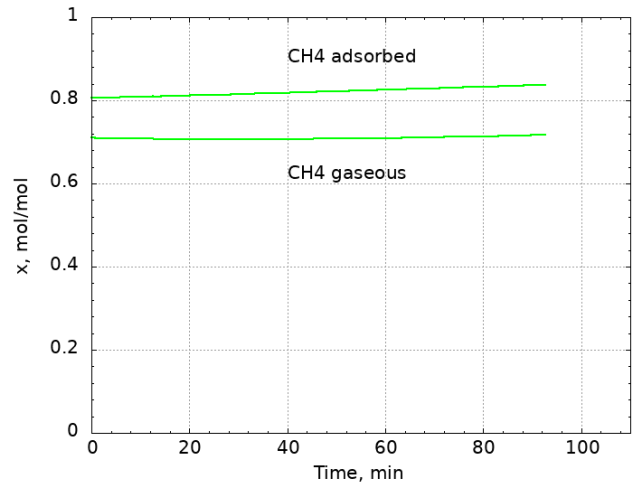
Fig. 9. Charging of a 33 litre adsorption tank with a methane-carbon dioxide mixture, concentration in the gas phase and in the adsorbed phase.
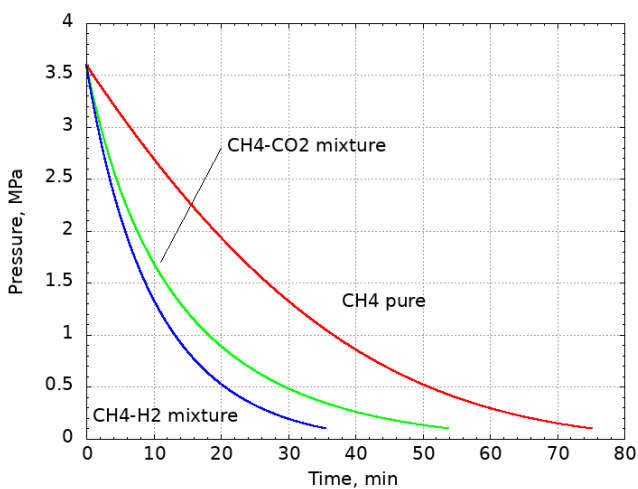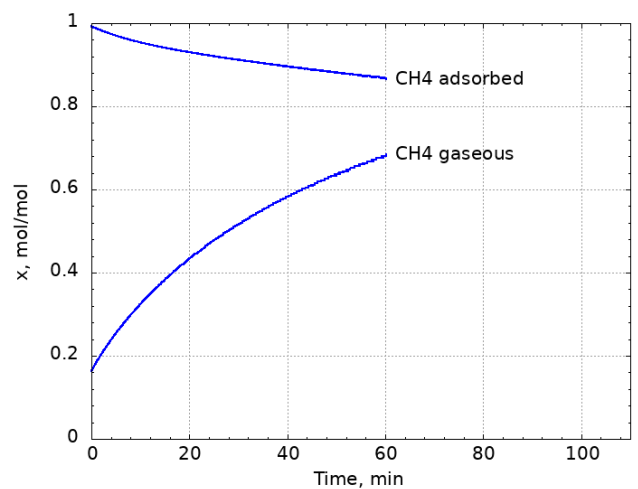

Fig. 10. Charging of a 33 litre adsorption tank with a methane hydrogen mixture, concentration in the gas phase and in the adsorbed phase.
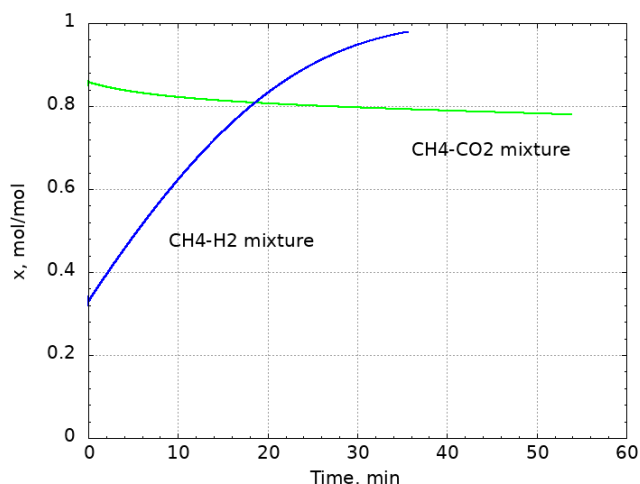
Fig. 11. Discharging of a 33 litre adsorption tank with a methane-carbon dioxide mixture and a methane-hydrogen mixture, concentration of the discharged gas mixture.

IV. DISCUSSION

The charging and discharging of methane, enriched methane (mixture methane - hydrogen) and biogas (mixture methane - carbon dioxide) is investigated. For many applications generic cylindrical tanks (i.e. 33 litre tank, height 1.19 m, diameter 0.229 m) might be used without any further provisions with regard to heat management as the heat transfer provided by natural convection is sufficient.

Due to the shift in the adsorption equilibrium during the discharge process the concentration of the outflowing gas mixture is varying. For enriched methane these variations significantly influence the energy content of the discharged fuel. For biogas an accumulation of carbon dioxide in the adsorption tank may occur.

The adsorption equilibria are strongly influenced by the model used and the model constants. Thus the results of this analysis with regard to mixtures are subject to future experimental verification. Nevertheless the qualititative outcome is viable.

Further scenarios with varying tank geometries, adsorbent materials, heat management mechanisms, mixture concentrations, maximum pressure levels and mass flux can be investigated using this approach. Thus an optimum combination for the adsorption gas mixture storage of a specific gas mixture can be found.

The assumption of constant area averaged temperature and pressure and of equilibrium might not hold if the charge

and discharge rates are very high. The numerical model might be extended accordingly.

Adsorption gas storage is a viable option for gaseous green fuels. Further analysis is needed to fully assess the peculiarities of adsorption storage of gas mixtures.

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