CO₂ recycling for Power to Gas using an amine-based sorbent

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Abstract

In the transition towards a more sustainable and CO₂ neutral energy system, Power to Gas concepts can play an important role. Especially in countries and cities with an extensive natural gas grid, this seems a convenient way for a smooth energy transition, in which fossil natural gas is slowly phased out and renewable natural gas from biogas and CO₂ methanation is increasingly blended in. In this work, the concept for a C-neutral gas recycling loop is introduced, based on CO₂ capture from flue gas of a gas fired boiler, methanation of the captured CO₂ and recycling this to the same boiler. For the capture part a fixed bed contactor was selected for complete CO₂ removal and producing pure CO₂ during regeneration. The performance of a commercial sorbent in an existing fixed bed contactor was tested and analyzed. Complete CO₂ removal and production of pure CO₂ for methanation was demonstrated. However, from these experiments it also became clear that the thermal conductivity of the sorbent bed was a limiting factor for maximizing the productivity of the system. A mathematical model of the reactor seems reasonably well capable of describing the systems performance and can be used for design of an improved system. Recycling CO₂ in a closed loop system needs further demonstration and evaluation.

Keywords: CO₂, recycling, power to gas, energy transition

1. Introduction

The capture and reuse of carbon dioxide via synthetic natural gas provides an elegant way of making a smooth energy transition from fossil natural gas driven applications (like heating, cooking) to systems driven by renewable electricity (from wind, solar, geothermal etc.), without requiring immediate replacement of associated equipment. The targeted system is schematically introduced in Figure 1. In this way, in the ideal situation, a closed loop CO2 recycle system is obtained.

To develop such a system, the process for CO₂ capture from the flue gas should be reliable (for stand-alone operation), energy efficient, delivering pure CO₂ without significant O₂ slip to the CO₂ methanation system and having a high capture efficiency. Small losses of CO₂ could be compensated for using direct air capture in either the same contactor or with an additional (lower pressure drop) air-sorbent contactor.

For efficient, small scale CO_2 capture a sorbent based process, using supported amines as active sorbent, seems an attractive option [1]. In this study the development, design and testing of a small scale system for CO_2 capture from real flue gas (from small scale boiler) using a commercial available amine based sorbent is presented. For stand-alone operation a fixed bed contactor was selected as basis for the capture process. Sorbent circulation is in principle more energy efficient [1], but also more prone to operational issues requiring operator attention and hence, seems more suited for larger scale applications. In the following sections subsequently sorbent properties and contactor design and testing will be presented.

Electricity   +   water & CO_2 from air = Sustainable Natural Gas
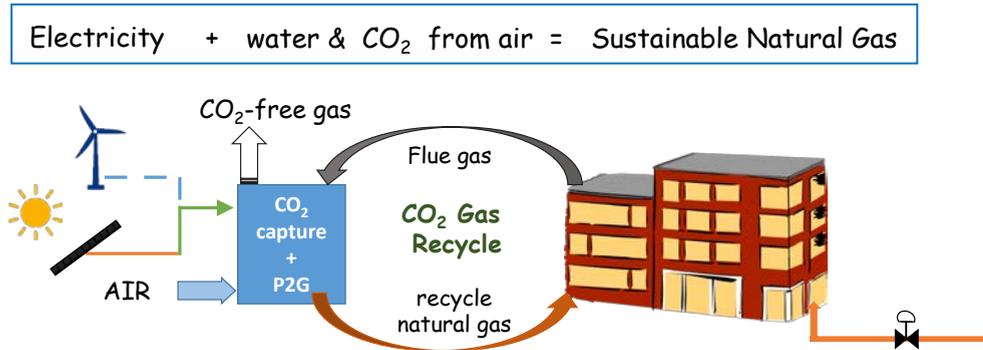
Figure 1. Concept for CO_2 Capture and Recycling for a smooth energy transition

Nomenclature

A	area	(m^2)
C	concentration (gas phase)	(mole/m^3)
C_P	specific heat	(J/kg K)
D	Diffusion coefficient	(m^2/s)
ΔH	Sorption enthalpy	(J/mole)
J	heat flux	(W/m^2)
q	molar capacity	(mole/kg sorbent)
r	radial position	(m)
R	radius of reactor	(m)
t	time	(s)
T	Temperature	(K)
U	overall heat transfer coefficient	(W/m^2 K)
v	linear gas velocity	(m/s)
x	cartesian coordinate	(m)
y	cartesian coordinate	(m)
z	cartesian coordinate	(m)
ε	bed porosity (gas fraction)	(-)
ϕ_v	volumetric gas flow rate	(m^3/s)
λ_{eff}	effective thermal conductivity of the sorbent bed	(W/m K)
ρ	density	(kg/m^3)

Subscripts

S	sorbent
G	gas phase

2. Materials and methods

2.1. Sorbent

For CO_2 capture the sorbent used is Lewatit VP OC 1065 from Lanxess, which has a polystyrene backbone with benzyl amine functional groups (primary amine groups) and is cross-linked with divinylbenzene. The CO_2 and H_2O adsorption equilibrium capacities have been reported elsewhere [2,3]. Whereas in cited studies the capture (adsorption) process was the main objective, here the production of pure CO_2 as feed for the methanation section is equally important. The methanation section itself was not investigated experimentally in the present study. The sorbent bed density (dry conditions) was determined to be 533 ($\pm$ 3) kg/m^3.

2.2. Contactor

The (existing) fixed bed contactor (0.15 m ID) used in the experiments is presented in Figure 2. The sorbent bed contained ca. 9.0 kg of sorbent during the experiments and can maximally contain 10.4 kg. It contains 20 heating/cooling pipes (4 mm ID / 6 mm OD) through which alternating cold water (during adsorption) or hot compressed water (during regeneration) can be led.
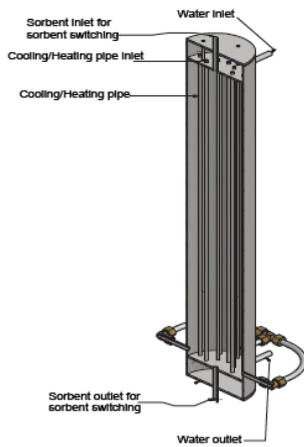
Figure 2. Fixed bed adsorber used in the experiments   Figure 3. Flue gas production (boiler CW1), compression and storage
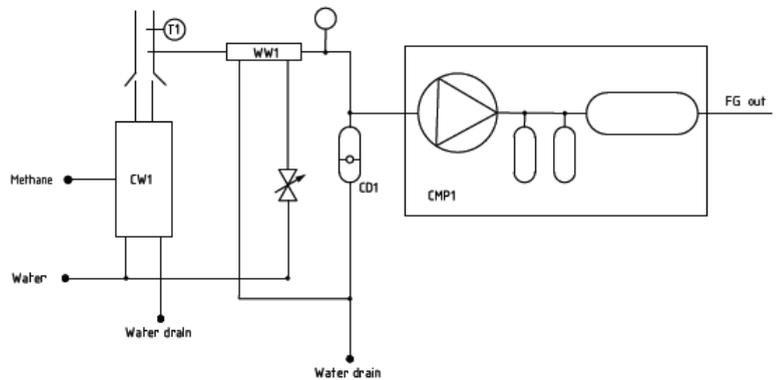
In Figure 3 the flue gas production is shown. A standard kitchen boiler is used and part of the exiting flue gas, along with some ambient air is sucked into the system by the compressor, dried and compressed to 7 bar. The final flue gas composition as determined from the gas leaving the intermediate buffer vessel after the compressor CMP1 is presented in Table 1.

Table 1. Flue gas composition (as measured).

Compound	Value	Units
CO_2	6.1	% (v/v)
O_2	9.8	% (v/v)
NO_2	129	ppm
NO	12	ppm
dewpoint	-20	°C

For the CO_2 product gas composition it is required that the oxygen content in the CO_2 product gas is significant

less than the lower explosion limit for O_2 in methane (4.6%) to avoid risks in the methanation section.

2.3. Sorbent thermal properties

As part of this study the thermal conductivity of the sorbent bed was determined. This was done using a double-walled, 1.2 L cylindrical vessel (see Figure 4), where the bottom and cylindrical wall are heated with a glycerol-water mixture as heat transfer fluid in a closed loop with a Julabo F32-HD heater. By measuring the temperature as a function of process time at different positions in the bed, indicated by the blue dots in Figure 4, during the transient heat transfer process and by comparison with a model for instationary heat conduction in a cylinder, the effective thermal conductivity for the bed of sorbents, and with that of the sorbent itself, can be determined. All thermocouples were logged at a one second time interval using a TC-08 data logger in combination with PicoLog. The environmental temperature is also measured.
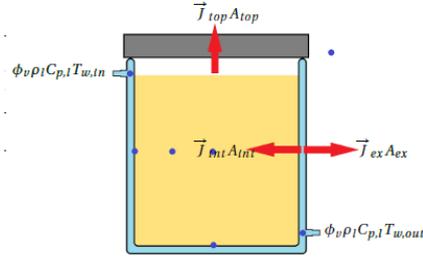
Figure 4. Determining the effective thermal conductivity of the sorbent bed

Prior to use the sorbent was dried at 50°C for 48 hours under N_2 to eliminate water and CO_2. The sorbent was transferred to the vessel directly after drying was completed. The vessel lid was sealed to avoid further contact between sorbent and environment, minimizing sorption effects during the heat transfer experiments. To ensure a homogeneous sorbent temperature the reactor is kept at a temperature of 20°C for 18 hours before measurements were started. At the start of a typical measurement the circular heater is set to measurement temperature and the data logging is started. Measured temperatures were varied between 30 to 50°C. The hot fluid transfers heat to the sorbent volume. Since the location of thermocouples in known exactly, precise data on temperatures inside the sorbent bed over time is obtained. The heat transfer process in the cylindrical sorbent bed can be described using Eq.(1).

$$\rho_s C_{P,s} \frac{\partial T}{\partial t} - \frac{1}{r}\frac{\partial}{\partial r}\left[\lambda_{eff} r \frac{\partial T}{\partial r}\right] - \frac{\partial}{\partial z}\left[\lambda_{eff} \frac{\partial T}{\partial z}\right] = 0 \tag{1}$$

The temperature gradients measured can now be used to calculate λ_{eff} using the model presentation in Equation (1), using the boundary conditions presented in Table 2 and under the following assumptions:

- the sorbent bed is pseudo-homogeneous;
- the gas phase between the particles is stagnant (no significant free convection in this closed system)
- sorbent temperature at the vessel wall and bottom are equal to the inner wall temperature
- heating liquid has a constant temperature inside the double wall (in view of high circulation rate)

Table 2. Boundary and initial conditions used

No.	Boundary	Boundary Condition	Equation	Comment
1	Center axis	No flux	$dT/dt = 0$	Symmetry condition
2	Vessel bottom	Set temperature	$T = T_{water,\ hot}$	From exp. data
3	Vessel wall	Set temperature	$T = T_{water,\ cold}$	From exp. data
4	Vessel top	Flux	$dT/dt = (JA)_{top}/(\rho_S C_{P,s})$	Heat leak, fit from data

2.4. Continuous cycling between capture and regeneration

In the fixed bed with heating/cooling pipes, as described in section 2.2, continuous and automated operation of the capture process was realised. In this process the contactor operates sequentially in the following phases:

(1) Adsorption. In this phase flue gas is fed to the contactor and CO_2 adsorbs on the sorbent. Cooling water runs through the heat exchange pipes to absorb the heat evolved during the exothermic adsorption. The adsorption phase ends when there is a 'breakthrough' of CO_2 in the gas phase at the exit of the column.

(2) Purge. At the end of the adsorption phase, flue gas containing oxygen is still present in the column. A short purge step with N_2 to replace the interstitial gas, and during which the purge gas is vented, can be implemented to avoid transport of oxygen to the CO_2 product gas during regeneration.

(3) Desorption. During the desorption phase hot water (95°C) runs through the tubes to heat the sorbent bed and to release the CO_2 adsorbed from the sorbent. A vacuum pump is installed and can be used to further lower the pressure during regeneration and to transport the CO_2 from the capture unit to the methanation unit.

(4) Cooling. After desorption is completed, when no more CO_2 leaves the column, a cooling step is required before the (exothermic) adsorption phase can be started. This is especially important since the presence of oxygen during adsorption leads to enhanced sorbent degradation when the temperature is (still) above 70°C. [4]

A PLC unit was used to switch the various valves in the flow scheme to control heating and cooling of the contactor via the heat exchange tubes inside the bed and to control the flow of the gases (feed and withdrawal). The time durations for each phase depend on process setting (such as temperature) and were finetuned manually, after which the continuous cyclic operation was continued automatically. Details of the setup can be found elsewhere [5]. Approximately, the duration of the adsorption phase was 20 minutes and the desorption time around 40 minutes. The incoming and outgoing gas streams to the contactor are analysed continuously for CO_2, O_2, NO_2, NO content, for dewpoint, flow, pressure and temperature.

For the desorption phase, next to runs without purge gas and using (recycled) CO_2 as purge gas, some reference experiments using N_2 as purge gas were carried out. These experiments allowed for checking the adsorption capacity of the sorbent bed, since the N_2 flow into the contactor is known, as well as the CO_2 content of the gas leaving the contactor. These reference runs with N_2 were carried out with a sorbent loading of 3 kg inside the contactor (approximately 30% of maximum contactor capacity).

2.5. Modeling the cyclic capture process

Like for the thermal conductivity measurements, section 2.3, the adsorption and desorption process in the contactor was modelled taking both mass transfer (CO_2 adsorption) as well as the thermal effects (heat transfer to/from the tubes and the exothermicity of the adsorption reaction) into account. Using Matlab's solvepde finite element solver, the time-dependent temperature, sorbent loading and CO_2 concentration as function of the location in the adsorber bed was modelled and compared with experimental obtained data, based on the geometry (Figure 2) as discretized in Figure 5.

(blue circles = heating pipes of contactor used, red circles = heating pipes of optimized size)
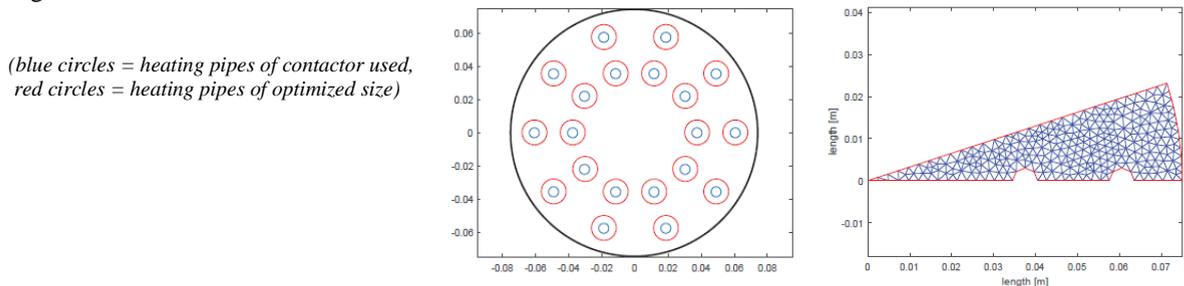
Figure 5.   (A) Reactor top view   (B) discretization grid for modelling

For describing the time-dependent adsorption process the gas phase and sorbent phase CO_2 mass balance and temperature balances are formulated and solved on the grid shown in Figure 5B. The energy balances for the gas and sorbent phase are presented in Eq.(2) and (3), the adsorption rate in equation (4) and the gas phase mass balance is listed in equation (5).

$$\varepsilon \rho_G C_{P,G} \frac{\partial T_G}{\partial t} = v_{G,z} \rho_G C_{P,G} \frac{\partial T_G}{\partial z} + \lambda_{G,x} \frac{\partial^2 T_G}{\partial x} + \lambda_{G,y} \frac{\partial^2 T_G}{\partial y} + \lambda_{G,z} \frac{\partial^2 T_G}{\partial z} + U_{S,G}\left(T_G - T_S\right) A_S \tag{2}$$

$$(1-\varepsilon)\rho_S C_{P,S} \frac{\partial T_S}{\partial t} = \lambda_{S,x} \frac{\partial^2 T_S}{\partial x} + \lambda_{S,y} \frac{\partial^2 T_S}{\partial y} + \lambda_{S,z} \frac{\partial^2 T_S}{\partial z} - U_{S,G}\left(T_G - T_S\right) A_S + \Delta H \frac{\partial q}{\partial t}(1-\varepsilon)\rho_S \tag{3}$$

$$\frac{\partial q}{\partial t}\left(1-\varepsilon\right)\rho_S = k \cdot C_G \cdot \left(q_{eq} - q\right) \qquad\qquad [1] \tag{4}$$

$$\frac{\partial C_G}{\partial t} = \frac{\partial q}{\partial t}\left(1-\varepsilon\right)\rho_S + \phi_v \frac{\partial C_G}{\partial z} + D_{eff,x} \frac{\partial^2 C_G}{\partial x^2} + D_{eff,y} \frac{\partial^2 C_G}{\partial y^2} \tag{5}$$

In above equations all thermal conductivities were taken equal to the effective thermal conductivity, as determined in this work. For the adsorption isotherm and kinetics the initial results by Veneman were used [1]. For the boundary conditions it is assumed that at the reactor wall there is no radial flux of CO_2, nor heat. At the walls of the heating pipes, the heat transfer is described by an overall heat transfer coefficient. Its value is both fitted by comparison with experiments (leading to U = 28 W/m^2 K) and estimated via heat transfer correlations (leading to U = 25 W/m^2 K). The sorbent to gas heat transfer coefficient is estimated using Nusselt correlations for convective flow in a fixed bed [5]. Using a few simplifying but justifiable assumptions, such as neglecting axial conduction, calculating the operational performance of the contactor with this 3D model (with rotation symmetry) is now possible in Matlab [5]. Typical CO_2 concentration profiles and temperature profiles are shown in Figure 6 a,b. Especially the temperature profile shows that temperature excursions can be quite significant during adsorption.
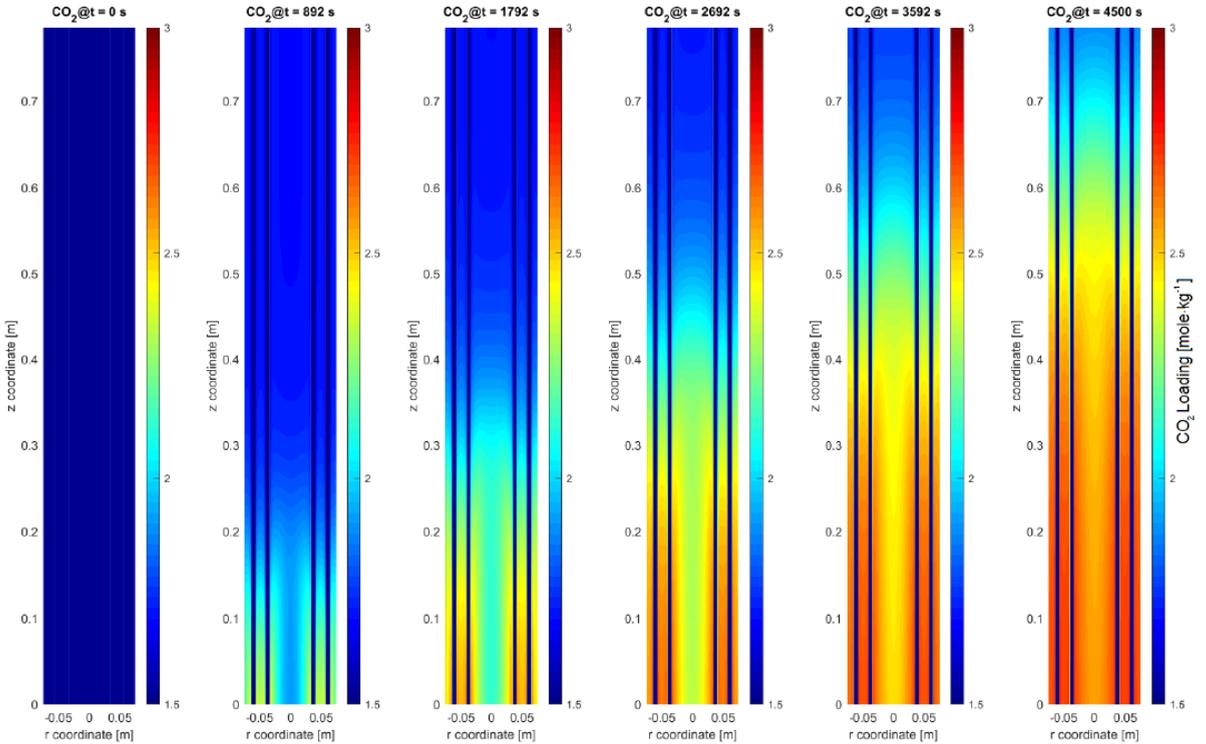
Figure 6a   Typical axial CO2 concentration profile during adsorption
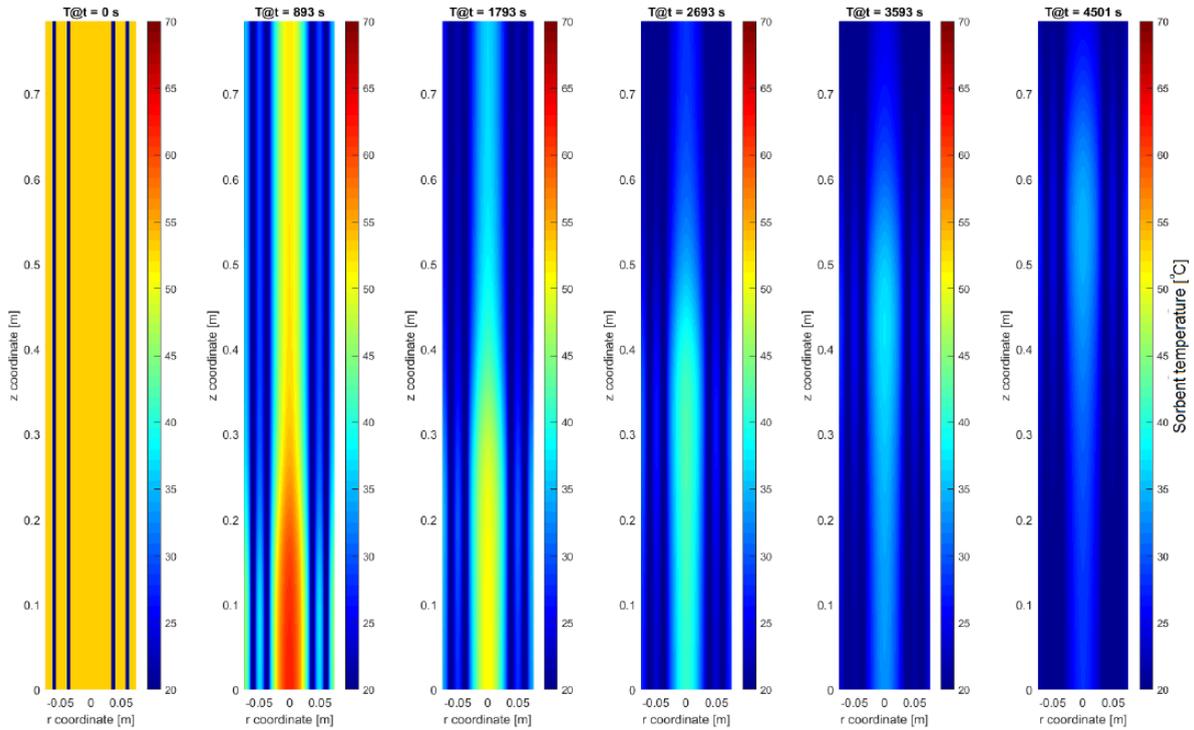
Figure 6b   Typical axial temperature profile during adsorption

3. Results

3.1. Sorbent thermal conductivity

Using the method described in section 2.3, the thermal conductivity of the sorbent bed is determined. The model implemented in Matlab, based on Eq.(1), described the transient warming up of the bed. The unknown parameters in the model (the effective thermal conductivity λ_{eff} and the heat loss to the environment from the top $(JA)_{top}$) were fitted, based on the measured temperatures inside the bed at the four indicated locations (Figure 4). With this, an excellent description of the experimental data was obtained, as evidenced by Figure 8.
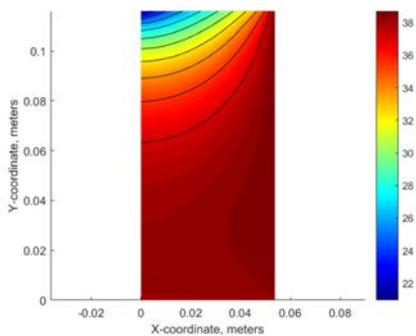
Figure 7. typical reactor temperature profile (T_{hot} = 40 ℃)
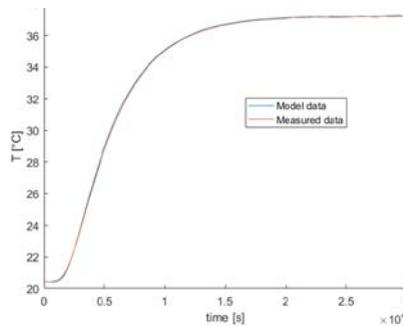
Figure 8. Model comparison vs. exp. data for mid of bed temperature.

Experiments at heating fluid temperatures of 30°C (2 exp.), 40°C (6 exp.) and 50°C (2 exp.) were carried out. When assuming the specific heat $C_{P,s}$ to be 1500 J/kg K [6], the thermal conductivity λ_{eff} found by the model is 0.113 W/m K at 30°C, 0.115 W/m K at 40°C and 0.117 W/m K at 50°C. Considering the thermocouple accuracy ($\pm$ 0.05°C) and the margin in thermocouple position ($\pm$0.001 m), the estimated error in λ_{eff} as found by the model is $\pm$ 0.008 W/m K. Since this error exceeds the observed, but minor, temperature dependency of λ_{eff}, a constant value of 0.115 ($\pm$ 0.008) W/m K is taken in further reactor analysis.

The effective thermal conductivity of a bed of particles is normally related to contributions from direct contact of the the (sorbent) particles, by gas conduction and by transport via radiation. The sorbent used in this work is polystyrene based and it is expected that the values found here for the effective conductivity should be reasonably in line with those for polystyrene particles. Reported thermal conductivities for different types of polystyrene (as homogeneous material) range from 0.15-0.22 W/m K. With these values, values of 0.09 – 0.14 W/m K are found for the effective thermal conductivity for a bed of polystyrene particles according to different correlations [5]. It can be concluded that the value of 0.115 W/m K determined in this work is well in line with literature estimates, based on polystyrene.

3.2. Fixed bed results and comparison with model

With the fixed bed unit continuous operation for several days was carried out. The results for a single cycle are shown in Figure 9 below. From the CO_2 production rate and the rate of temperature change it was clear that (i) temperature excursions during adsorption are significant; (ii) heat transfer (heating during desorption and cooling afterwards) is slow and limiting system productivity and, therefore, (iii) fluidization (in a fixed fluid bed mode) is worth considering in view of improving heat transfer.
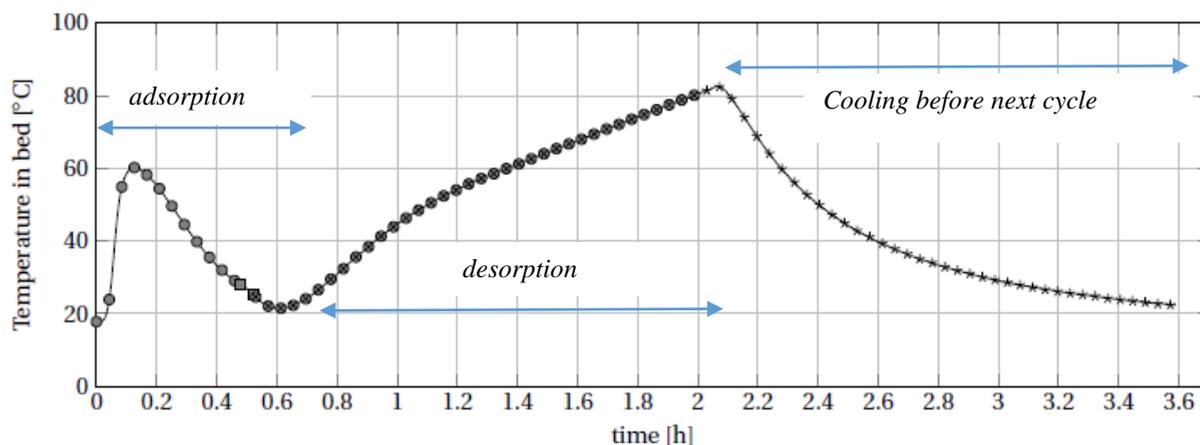
Figure 9 Temperature profile (in the center of the bed) during a single adsorption/desorption cycle.

With the model, one of the experimental runs (not the one in Figure 9) is simulated to compare the performance calculations based on the model, with those actually obtained with the fixed bed reactor. The comparison of a few characteristic parameters is presented in the table below and shows that despite the uncertainties involved in the parameters, the overall performance is reasonably well predicted by the model. In Figure 10 a parity plot is presented for the modelled and the experimental determined temperatures (in the center of the reactor (circles) and between inner and outer cooling pipes (squares)).

Table 3. Model vs. experiment

Parameter	Unit	Experiment	Model
Productivity	mole CO_2 h^{-1}	2.51	2.46
Breakthrough time	s	3700	3778
Working capacity	mole kg^{-1}	0.78	0.74

As mentioned above, heat transfer seems to be limiting the system productivity for contactor used in this study. By modelling, a good compromise for increasing the system productivity (mole CO_2 captured per m^3 contactor per day) by changing the tube diameter can be found, see Figure 11. The optimum is also indicated by the red circles in Figure 5. The adsorber could be further optimized by changing the amount of tubes and the tube arrangement inside the bed.
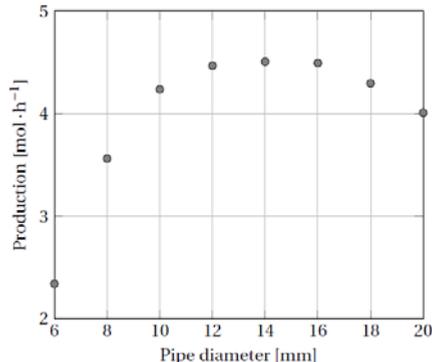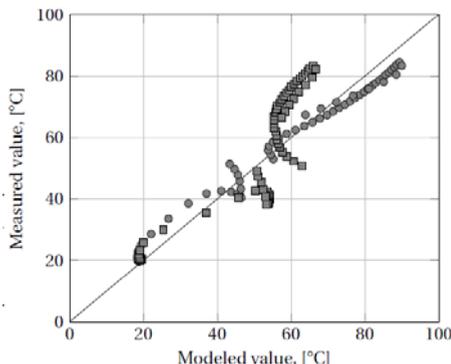
Figure 10   Parity plot of temperatures in center (circles) and between pipes (squares)   Figure 11 Optimum tube diameter for same contactor

With respect to capture performance; essentially all CO_2 in the flue gas was captured since 'no CO_2' (in any case much less than 1%) was detected in the treated flue gas. The CO_2 produced during regeneration appeared to be quite pure; no GC analysis was made, but the oxygen detector indicated that there was no O_2 slipping to the product gas. For NO_2 (typically present at a level of 130 ppm in the flue gas) and NO (12 ppm in the flue gas), additional efforts are needed since NO_2 nor NO was detected in the product gas, but remarkably also not in the treated flue gas.

4. Conclusion

In this work a lab scale unit for CO_2 capture from flue gas from a gas-fired boiler, by using a fixed bed with a supported amine sorbent has been tested and a model was developed to describe its performance. The preliminary agreement between model and experiments was good. Near complete (100%) CO_2 recycle seems feasible and oxygen slip to the methanation section seems negligible. The model needs further confirmation under different conditions, but preferable in combination with an optimized experimental configuration as heat transfer is limiting the current one. The model enables further optimization and an improved design of the system. The concept proposed of CO_2 capture from flue gas and recycling via power to gas is a concept worthwhile considering as transition technology.

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