



13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18
November 2016, Lausanne, Switzerland

Design strategy for CO₂ adsorption from ambient air using a supported amine based sorbent in a fixed bed reactor

Q. Yu*, D.W.F. Brilman

Sustainable Process Technology Group, Faculty of Science and Technology, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

Abstract

In this work, a fixed bed reactor is evaluated for CO₂ capture from ambient air using an amine based ion exchange resin. Using adsorption experiments, the effect of superficial velocity and bed length on process economics is investigated. It is shown that the optimal conditions are found at an adsorption duration of 0.5–1.5 times the stoichiometric time for sorbent loading. To reduce pressure drop during adsorption, a radial flow reactor is proposed and designed for capturing CO₂ from ambient air.

© 2017 The Authors. Published by Elsevier Ltd.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: CO₂; air capture; amine sorbents; adsorption; fixed bed

1. Introduction

CO₂ is the main greenhouse gas (GHG), responsible for over 82.5% of total GHG emission. The concentration of CO₂ in atmosphere has increased of ca. 100 ppm from pre-industrial period to 2007. The level of CO₂ will reach 550 ppm by 2050 with the current rate of emission [1]. This increase of CO₂ level predominantly originates from anthropogenic emissions. According to the IPCC, around half of the anthropogenic emission of CO₂ emission come from distributed sources such as auto vehicles, aircrafts and heating systems in buildings [2]. Under these circumstances, capturing CO₂ from air (“air capture”) is gaining interest as it is considered as ultimate technology to mitigate anthropogenic emission of CO₂ from dispersed sources. Capturing CO₂ from air is independent on the

* Corresponding author. Tel.: +31-53-489-4635; fax: +31-53-489-4738

E-mail address: q.yu-2@utwente.nl

source of CO₂ and provides high flexibility on the choice of location. The captured atmospheric CO₂ can be utilized as carbon source for e.g. storing excess renewable electricity in the form of methanol and for algae cultivation. The latter has been identified as potential source for not only fuel production, but for a wide range of consumer products.

One popular method for capturing CO₂ from flue gas is based on aqueous amine solutions. These solutions are widely used to capture CO₂ from high CO₂ content gases, but are less suitable for CO₂ capture from ambient air since the amine compounds responsible for capturing the CO₂ deactivate rapidly when in contact with (dissolved) oxygen at regeneration conditions. Moreover, for CO₂ air-capture there will be a significant solvent loss via evaporation since the solvent needs to be in contact with a massive amount of air [3].

These limitations are largely overcome using amine-functionalized solid sorbents. For these solid amine sorbents it is generally assumed that they react along similar reaction pathways as for aqueous phase amine systems. An important advantage is that less energy is needed in the form of sensible heat as heating up the bulk of the water as solvent is avoided. The solid amine sorbents applied in a gas-solid process, are said to possess other advantages such as much faster sorption kinetics as liquid phase diffusion is avoided, higher CO₂ capacity, higher stability, higher resistance to contaminants and less emissions [4, 5]. The feasibility of capturing CO₂ from air using solid amine sorbents has already been proposed and confirmed by several studies [6-10]. Whereas for physical CO₂ sorbents the presence of water vapor can be detrimental, for amine-based sorbents the capacity of CO₂ even increases in humid air, compared to dry air [11].

Having solid amine sorbents identified as a promising candidates to capture CO₂ from air [10], the next step is to realize this in a practical, technical feasible and economic viable operation. Taking into account the low concentration of CO₂ in air and the low product price, this is a real challenge! Since there is only 400 ppm CO₂ in air, a huge amount of air is required to supply enough CO₂ to saturate the sorbent, making any reactor type leading to large pressure drop unfavorable. Evaluating the cost and feasibility of capturing CO₂ from air with solid amine sorbents is still in an early stage. In literature, only very few studies on process- and reactor design for CO₂ air capture are available which discuss to some extent reactor selection, cost estimation and optimization of some operating parameters such as adsorption time, gas velocities, energy for contacting, gas/solid efficiency and sorbent regeneration.

Kulkarni et al. estimated on basis of a theoretical study that the operational cost of capturing CO₂ from air using an amino-modified silica adsorbent in a structured monolithic reactor around 100 \$/ton CO₂ avoided [12]. Brilman and Veneman estimated for a plate-type adsorber on basis of experimental adsorption capacities and cost estimations for amine-impregnated sorbent, contactor and operational costs a total cost of 150-200 \$/ton CO₂, including operational costs of around 55 \$/ton CO₂ [10]. Zhang et al. tested a PEI-silica adsorbent in a bubbling fluidized bed to capture CO₂ from air. On the basis of their experimental results in bubbling fluidized bed, a conceptual design for CO₂ air capture was proposed and estimated the operating cost to be 152 \$/ton CO₂ avoided [13].

For gas-sorbent systems, the required duration in the adsorption phase plays a significant role. Choosing a short sorption time enables more loading/unloading cycles per day (a higher productivity [kg CO₂/day]) and reduce sorbent costs, but on the other hand lead to incomplete sorbent saturation, and hence to inefficient sorbent usage and higher energy requirements per unit of CO₂ captured. For the ion exchange resin studied in this work, initial work by Smal et al. [14] showed that the adsorption time required to saturate the particles under CO₂ air capture conditions is in the range of hours rather than seconds. Hence, process- and gas-solid contactors based on solids circulation with short particle residence times and low sorbent holdup seem not attractive and are excluded from this study.

Two of the main challenging and partly conflicting conditions in capturing CO₂ from air include sufficient CO₂ supply (at 400 ppm in air) and minimizing pressure drop during adsorption. Pressure drop is an essential parameter as it is directly related to the energy consumption ($E = \varphi_v \cdot \Delta P$) for gas-sorbent contacting. Handling large amounts of gas for CO₂ air capture is inevitable, since around 1400 m³ of ambient air is needed per kg of CO₂. Due to this, the pressure drop over the gas-solids contactor for CO₂ capture from air should be much lower than for other CO₂

capture processes. Only contactors which can realize a low pressure drop are viable for CO₂ air capture. Based on pressure drop considerations, we will firstly select the type of reactor between the fixed bed family and the fluidized bed family. The pressure drop for a fluidized bed reactor is calculated via the gravity of the solid minus the buoyancy force [15, 16].

$$\Delta P = (\rho_s - \rho_f) \cdot (1 - \varepsilon) \cdot g \cdot L \quad (1)$$

The pressure drop for a fixed bed, assuming spherical beads, can be estimated by the Ergun equation [15].

$$\frac{\Delta P}{L} = \frac{150\eta(1-\varepsilon)^2}{\varepsilon^3 d_p^2} u_f + \frac{1.75\rho_g(1-\varepsilon)}{\varepsilon^3 d_p} u_f^2 \quad (2)$$

Pressure drop in both Eq. (1) and (2) is proportional to the length of the bed L . Therefore, a small height of the bed, in the order of magnitude of several centimeters, is the key to realize a low pressure drop. For a fluidized bed, it seems highly impractical for a very shallow bed to fluidize the solids as well as maintain a uniform gas distribution. Non-uniform gas distribution will lead to local bypassing of the sorbent bed, which decreases the gas removal efficiency. Furthermore, for very shallow beds the pressure drop over the gas distributor is significant, sometimes even larger than the pressure drop over the bed itself [16]. In contrast, a high-pressure drop gas distributor is not needed in case of a fixed bed reactor. We therefore anticipate here that a fixed bed contactor is a more attractive option for CO₂ air capture as it is possible to operate with a small bed height.

In our previous work, we tested an amine based ion exchange resin on its feasibility to capture CO₂ from air. The experimental results show that this adsorbent enjoys a high CO₂ capacity and relative moderate water capacity during CO₂ capture from air [14]. Next to CO₂ adsorption capacity at different temperatures, there are still some parameters required for an optimum reactor design. Especially, optimization of the duration of the adsorption and the solid efficiency during adsorption are important. These two parameters are important as they determine the total amount of sorbent required (and the sorbent capacity per day) and the sorbent cost and energy efficiency of the process.

In this work, these parameters will be determined through experimental work on CO₂ adsorption in a fixed bed contactor. Although the experiments were performed for a specific solid amine sorbent, the approach followed is likely to be applicable to other (amine-based) sorbents as well. Several important process parameters such as sorbent use efficiency, gas capture efficiency and adsorption time will be evaluated and optimized in terms of their influence on the process economics. From the experimental findings, guidelines for process- and reactor design for CO₂ air capture are developed and will be presented.

2. Experimental

2.1 Material

The sorbent material used in this study is Lewatit VP OC 1065, a commercial ion exchange resin (IER) composed of primary amine functionalized polystyrene. The total amine loading, as measured by Alesi et al. [17] via Energy-dispersive X-ray spectroscopy (EDS) is 7.5 mole/kg. The resins beads are spherical with a diameter between 0.3 mm and 1 mm. The pore volume, surface area and pore diameter of the IER were measured to be 0.2 cc/g, 25 m²/g and 38 nm respectively.

2.2 Experimental set-up

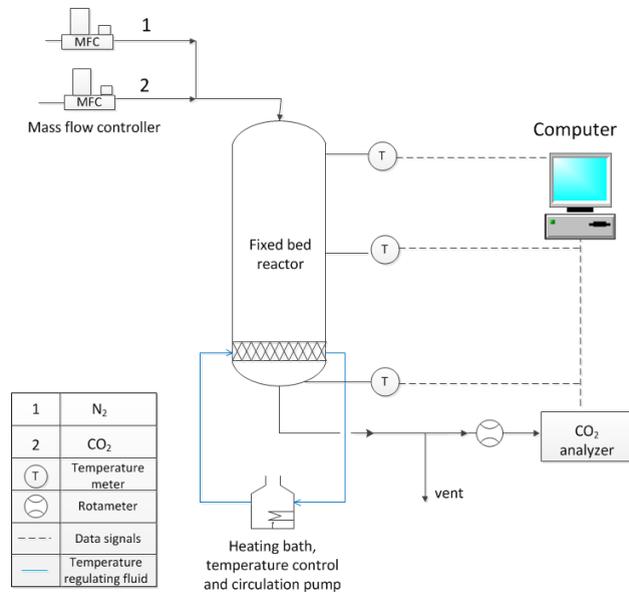


Fig. 1. Schematic diagram of lab-scale fixed bed reactor

The experimental work focuses on the CO₂ adsorption at ambient condition at various superficial velocities. For this purpose, a lab-scale fixed bed reactor was used to assess the process. The internal diameter and length of the reactor is 0.016 m and 0.50 m. A schematic of the set-up is shown in Fig. 1. The CO₂ concentration in the ambient condition in the inlet gas was created by mixing a flow of high purity (grade 5.0) N₂ and a high purity (grade 5.0) CO₂. The flow rates were controlled using two BROOKS mass flow controllers. The set-points of two mass flow controllers were adjusted to reach different superficial velocities. The JULABO F32 water bath was used to control the temperature of the reactor in both adsorption and desorption process. The CO₂ analyzer (LI-COR LI840A) was used to monitor the CO₂ concentration in the outlet gas of the fixed bed reactor (detection range: 0–2 mole %). The uptake rate of CO₂ in the adsorption in the unit of mole kg⁻¹ s⁻¹ can be calculated from the measured CO₂ concentration in the outlet. Besides, there are three thermocouples connected to the top, middle and bottom part of the reactor, the temperature signals at these positions together with the CO₂ reading of the analyzer were recorded in the computer. In the adsorption process, 400 ppm of CO₂ was purged into the reactor under the superficial velocity of 0.05 – 0.3 m/s at the temperature of 25 °C with a loading of 1-3 g of sorbent. In the desorption process, pure N₂ was purged into the system under the flow of 0.21 m/s at 80 °C. Desorption stops when the CO₂ concentration in the outlet was below 10 ppm.

3. Methodology

3.1 Process parameter definition

The stoichiometric time is the minimum time required to reach the cyclic sorbent saturation capacity $q_e - q_{de}$ (in g/kg IER), and is defined as follows

$$t_{sto} = \frac{m_s \cdot (q_e - q_{de})}{\phi_v \cdot C_{CO_2}} \quad (3)$$

Here, m_{sorbent} represents the mass of the sorbent (kg), q_e represents the equilibrium capacity of CO₂ in the adsorption (g/kg_{IER}), q_{de} represents the capacity of CO₂ in the desorption (g/kg IER), ϕ_v represents the volumetric flow (m³/min) of the gas introduced to the reactor and C_{CO_2} represents the concentration of CO₂ in the gas entered the reactor (g/m³).

The gas capture efficiency of CO₂ ('gas efficiency') is calculated from the experimental determined CO₂ concentration in the gas leaving the reactor, using the following equation:

$$\eta_g = \frac{C_{CO_2,in} \cdot t - \int_0^t C_{CO_2,out} dt}{C_{CO_2,in} \cdot t} \quad (4)$$

The saturation efficiency of the adsorbent ('solid efficiency') is calculated as:

$$\eta_s = \frac{q_t - q_{de}}{q_e - q_{de}} \quad (5)$$

In Eq. (4), $C_{CO_2, in}$ and $C_{CO_2, out}$ represent the concentration of CO₂ in the inlet gas and outlet gas stream of the reactor. In Eq. (5), q_t (g/kg_{IER}) represents the adsorbed CO₂ capacity of the sorbent at adsorption time t .

The overall mass balance of the adsorption process:

$$\phi_v \cdot C_{CO_2,in} \cdot t = (q_e - q_{de}) \cdot m_s \cdot \eta_s + \phi_v \cdot C_{CO_2,out} \cdot t \quad (6)$$

The Eq. (6) can be reduced to:

$$\frac{t}{t_{sto}} = \frac{\eta_s(t)}{\eta_g(t)} \quad (7)$$

Where, t is the duration of the adsorption (min), η_s and η_g are the solid efficiency and gas capture efficiency.

3.2 Process economics

The evaluation (and optimization) of the adsorption duration is based on process economics, which include the cost of the sorbent, cost of the contacting energy and the regeneration energy.

The cost of the sorbent per ton CO₂ captured is calculated by

$$\dot{C}_{IER} \left[\frac{\text{€}}{\text{ton}_{CO_2}} \right] = \frac{C_{IER} \left[\frac{\text{€}}{\text{kg}} \right] \cdot m_{IER} [\text{kg}]}{Y_{cycle} [\text{g}] \cdot \dot{N}_{cycle} \cdot L_{IER} [\text{d}]} \cdot 10^6 \left[\frac{\text{g}}{\text{t}} \right] \quad (8)$$

Where C_{IER} is the cost of the sorbent, m_{IER} is the amount of adsorbent, Y_{cycle} is yield of CO_2 per adsorption-desorption cycle, \dot{N}_{cycle} the number of cycles per day and L_{IER} is the sorbent lifetime. The yield per cycle is calculated as

$$Y_{cycle}[g] = (q_e - q_{de}) \left[\frac{mole}{kg} \right] \cdot m_s[kg] \cdot M_{CO_2} \left[\frac{g}{mole} \right] \cdot \eta_s[\%] \quad (9)$$

Where M_{CO_2} is the molar mass of CO_2 , cyclic yield has strong relevance to the solid efficiency based on Eq. (9).

With the (conservative) assumption of the desorption time equals to the adsorption time, the number of cycles is calculated as

$$\dot{N}_{cycle} \left[\frac{cycles}{d} \right] = \frac{1440 \left[\frac{min}{d} \right]}{2 \cdot t_{ad}[min]} \quad (10)$$

Moving forward to the contacting energy, the contacting energy is calculated by

$$\dot{E} \left[\frac{J}{g} \right] = \frac{\Delta P[Pa]}{\eta_g \cdot C_{CO_2} \left[\frac{g}{m^3 air} \right]} \quad (11)$$

The pressure drop in Eq. (11) was calculated using the Ergun equation shown in Eq. (2), C_{CO_2} represents the mass of CO_2 per unit volume of air, here taken as 0.72 g/m^3 (400 ppm, at 1 atmosphere and 25°C).

The cost of the contacting energy, C_{con} , is calculated based on the Eq. (12):

$$\dot{C}_{con} \left[\frac{\epsilon}{t_{CO_2}} \right] = \frac{\dot{E} \left[\frac{J}{g} \right]}{3.6 \cdot 10^6 \left[\frac{J}{kWh} \right]} \cdot C_{elec} \left[\frac{\epsilon}{kWh} \right] \cdot 10^6 \left[\frac{g}{t} \right] \quad (12)$$

The cost for regeneration, C_{reg} , based on regeneration energy can be calculated through Eq. (13).

$$\dot{C}_{reg} \left[\frac{\epsilon}{t_{CO_2}} \right] = (H_{rx} \left[\frac{kJ}{g} \right] + \frac{C_{p,IER} \left[\frac{J}{kg \cdot K} \right] \cdot (T_{de} - T_{ad})[K]}{(q_e - q_{de}) \left[\frac{mole}{kg} \right] \cdot \eta_s \cdot M_{CO_2} \left[\frac{g}{mole} \right]}) \cdot \frac{1}{1000} \left[\frac{kJ}{J} \right] \cdot C_{therm} \left[\frac{\epsilon}{GJ} \right] \quad (13)$$

In equation (12) and (13) the energy costs C_{elec} and C_{therm} are respectively the costs for electric energy and thermal energy. H_{rx} and $C_{p,IER}$ are the heat of the reaction and the heat capacity of the solid. The regeneration energy in this study only considers the heat of reaction (H_{rx}) and the sensible heat to heat up the solid.

4. Results and Discussion

4.1. The effect of gas velocity and amount of sorbent

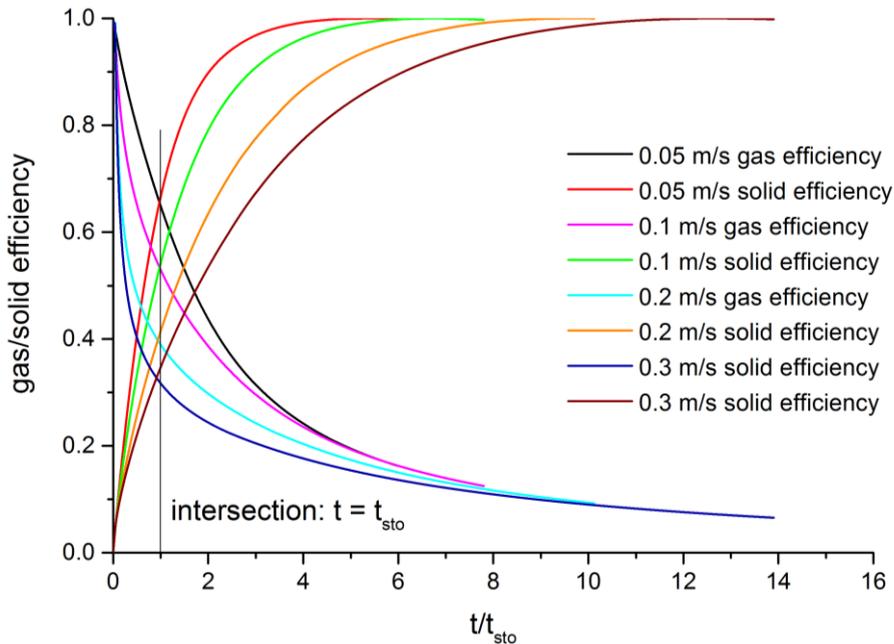


Fig. 2. Experimental obtained efficiencies η_s and η_g vs. (t/t_{sto}) ($P_{CO_2,in} = 40$ Pa, 1 g of sorbent)

The effect of superficial velocity was measured in fixed bed reactor with a loading of 1g of sorbent at different superficial velocities. The change of velocities results in altering the stoichiometric time according to Eq. (3). Fig. 2 shows the relation between η_s , η_g and t_{ads}/t_{sto} at superficial gas velocities of 0.05, 0.1, 0.2, 0.3 m/s at a temperature of 298K and at a CO_2 partial pressure of 40 Pa. The intersections of the experimental determined efficiency lines (where $\eta_s = \eta_g$) indeed appear at $t = t_{sto}$, which is in agreement with the theoretical derivation (in Eq. (7)). The stoichiometric saturation time t_{sto} represents the minimum time required to saturate the sorbent, which equals to 84, 42, 21 and 14 min respectively at $u_G = 0.05, 0.1, 0.2$ and 0.3 m/s.

The superficial velocity has an influence on the uptake rate of CO_2 , since the time to reach 80% saturation decreases from 120 min to 62 min when the gas velocity increase from 0.05 m/s to 0.3 m/s. The influence of superficial velocity is associated with CO_2 supply to the adsorbent. The CO_2 supply is proportional to the velocity when the CO_2 concentration of inlet gas is constant. Besides, an increase of adsorption time to reach 80% saturation of the adsorbent by a factor of 2 (from 62 to 120 min) instead of 6 (from $u_G = 0.3$ m/s to $u_G = 0.05$ m/s) indicates there is a certain extent of limitation from intra-particle diffusion or reaction kinetics. This finding is also supported by the value of η_s or η_g at $t/t_{sto} = 1$ decreases from 0.65 to 0.32 when the velocity increases from 0.05 m/s to 0.3 m/s. The intra-particle diffusion was related to the morphology of the adsorbent, and was reported to limit the uptake rate of CO_2 at low temperature (e.g. 25 °C) for several types of mesoporous solid amines [18, 19].

Fig. 3 shows the kinetics of CO_2 adsorption from ambient air of Lewatit 1065 in comparison to other solid amines. Here we present the comparison using the adsorption half time at different stoichiometric times. Adsorption half time is the time required to reach 50% of the maximum adsorption capacity. In the cited studies [6, 20, 21], the adsorption capacity of the sorbents, the flows and the amount of sorbents are different. Therefore, the adsorption half time is plotted in Fig. 3 versus the stoichiometric time, in order to normalize for differences in adsorption

capacity, amount of adsorbent and flow. This concept takes all of these into account and unifies the various experimental conditions among various adsorbents and studies. The adsorption half time of AEAPDMS-NFC-FC is 92 min, much longer than 55 min of the IER used in this study, while the stoichiometric time of both adsorbents are almost the same (81 min vs. 84 min). The stoichiometric times of various PEI/silica are similar to Lewatit at $u_G = 0.1$ m/s. The adsorption half time of A- PEI/silica is 196 min, the minimum among various PEI/silica adsorbents, nevertheless it still three times longer than Lewatit (43 min). Note that AEAPDMS-NFC-FC and HAS6 were studied at humid conditions. It is not clear from these references to what extent the CO₂ adsorption kinetics for these sorbents are influenced by the presence of water. Besides, PEI/silica were tested in thermogravimetric analyzer (TGA) while other adsorbents were tested in fixed bed reactor. There is probably mass transfer limitation to the sorbent at the bottom measured in TGA. According to Choi et al. [21], the adsorption half time of HAS6 was constrained by mass transport through the pores. The fast kinetics of CO₂ adsorption for current IER might be attributed to larger pores (38 nm) versus 4.9 nm for the HAS6 sorbent and the larger pore volume (0.2 cc/g vs. 0.11 cc/g respectively). Large pores is beneficial for permeability of CO₂ and accessibility of amine. Fig. 3 confirms that the IER used in this study, Lewatit 1065, shows good performance with respect to adsorption kinetics for capturing CO₂ from air and is worth further study in practical application.

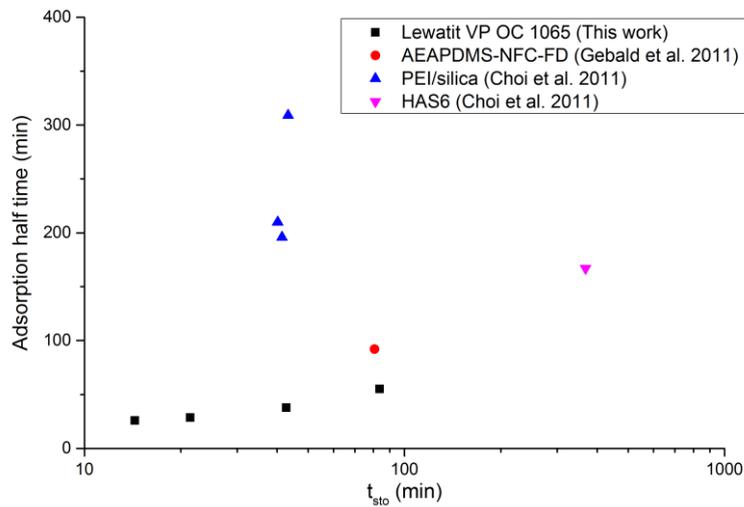


Fig. 3. Stoichiometric time vs. adsorption half time of different amine based sorbents for capturing CO₂ from ambient air.

Table 1: Parameters of calculation results shown in Fig. 4-5

Parameters	
Temperature of desorption T_{de} (K)	353.15
Temperature of adsorption T_{ad} (K)	298.15
Sorbent heat capacity $C_{p,IER}$ (kJ/kg/K) [22]	1.5
$q_e - q_{de}$ (gCO ₂ /kgIER) (298K, $P_{CO_2} = 40$ Pa)	40
Heat of reaction H_{rx} (kJ/g) [11]	1.7
Cost of thermal energy from natural gas C_{therm} (€/GJ) [23]	3.44
Cost of electricity C_{elec} (€/kWh) [24]	0.10
Daily operating time (h)	24
Cost of the IER C_{IER} (€/kg) (assumption)	13
Lifetime of the IER L_{IER} (y)	3.0

The choice of adsorption time determines not only the solid efficiency but also gas capture efficiency (see also Fig. 2), while both η_s and η_g are related to process economics. A high solid efficiency saves the cost of the sorbent and regeneration energy and a high gas efficiency reduces the cost of the contacting energy. However, the variation of the η_s and η_g with adsorption process time are opposite. A 100% gas efficiency can be reached at the initial stage when the sorbent is free from CO₂. On the other hand, a complete saturation of the solid is a time consuming process; the last 20% of saturation of the IER almost takes the double amount of adsorption time, thereby reducing enormously the amount of possible cycles per day. Hence, there is a trade-off between solid efficiency per cycle and number of cycles per day, making the choice for an optimum process time for adsorption a crucial process design variable.

We evaluated the choice of the adsorption time on the total cost of the process with the parameters listed in Table 1. The total cost contains cost of the sorbent, cost of the contacting energy and cost of the regeneration energy. According to Eq. (8), cost of the sorbent is related to the daily yield Y_d . Daily yield is obtained by the amount of CO₂ captured per cycle multiplied with the number of cycles per day. As what is shown in Fig. 4 (a), the yield per cycle increases with the increase of the adsorption time. However, the number of cycles per day decreases with the increase of the adsorption time. After multiplication of these parameters, there is a decrease of daily yield with increasing adsorption time because the average uptake rate of CO₂ decreases with an increase of adsorption time. The uptake rate of CO₂ is related to the CO₂ loading in the sorbent, it decreases when the loading of CO₂ in the sorbent increases. Since both the daily yield and the gas capture efficiency decrease with increasing adsorption time, there is an increase of the cost of both the sorbent and the contacting energy based on Eq. (8) and (12). However, the decrease of adsorption time is accompanied by a decrease in the solid efficiency. As a result, it consumes more energy (and leads to higher costs) to regenerate the same amount of CO₂.

Fig. 4 (b) displays the effect of adsorption time on the cost of the sorbent, the contacting energy and the regeneration energy for a selected superficial gas velocity of 0.3 m/s. The turning point / optimum occurs at $1.4 \cdot t_{sto}$, under the current assumptions and set of prices, accompanied with an operational cost of 58 €/t CO₂ captured. This cost contributes 28% to the electricity consumed in the contacting process and 38% to the heat requirement of the regeneration. The energy consumption on the electricity is 0.6 GJ/t CO₂ at 118.4 Pa of pressure drop and the thermal energy is 6.5 GJ/t CO₂, without any heat integration. As a comparison, Kulkarni et al. [12] estimated an amino-modified silica adsorbent air capture in monolith, and the process requires 0.8 GJ/t CO₂ of electricity and 6.0 GJ/t CO₂ of thermal energy. Hence, despite the entirely different contactor concept, the results from our analysis are in a similar range as those of Kulkarni et al. For the experiment with superficial velocities of 0.05, 0.1 and 0.2 m/s in air, the cost analyses shows similar trends, as can be seen in Fig. 5 (a). In Fig. 5 (a), the optimal costs at $u_G = 0.05 - 0.3$ m/s lay all in the range of 0.5-1.5 t_{sto} . The minimum overall cost (52 €/tCO₂) in the present study was found at $u_G = 0.2$ m/s, since it enjoys smaller pressure drop than $u_G = 0.3$ m/s as well as higher cyclic operating capacity than $u_G = 0.05$ m/s. Fig. 5 (a) shows that the choice of a proper velocity is crucial for the economics; operating at larger gas velocity saturates the adsorbent faster but gives rise to large pressure drop. However, small velocity has a smaller pressure drop, but leads to lower overall productivity due to a lower number of cycles per day. From the results discussed above, the optimum window for the gas velocity with a loading of 1 g of IER was found to be between $u_G = 0.1$ to 0.3 m/s.

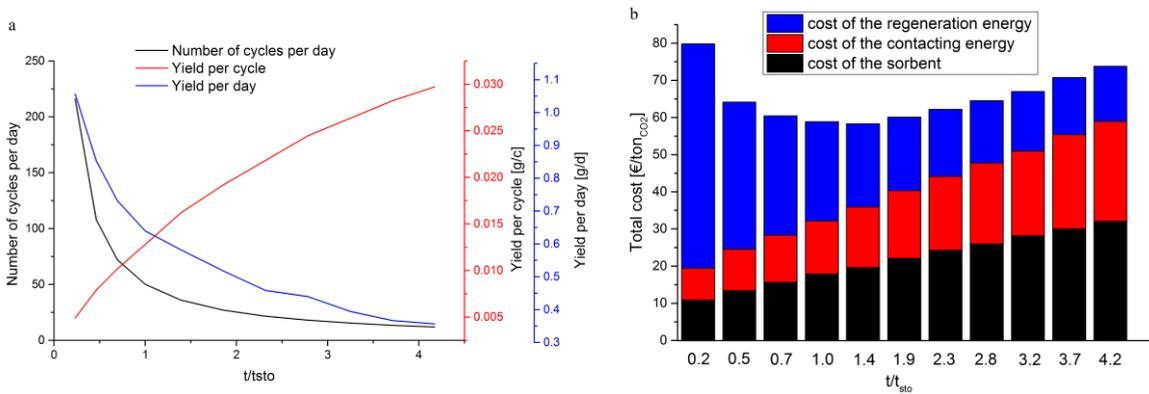


Fig. 4. (a) Number of cycles per day, yield per cycle and yield per day vs. adsorption time of loading 1 g of IER at $u_G = 0.3$ m/s. ($p_{CO_2} = 40$ Pa, 298 K); (b) Total cost vs. adsorption time of loading 1 g of IER at $u_G = 0.3$ m/s. ($p_{CO_2} = 40$ Pa, 298 K)

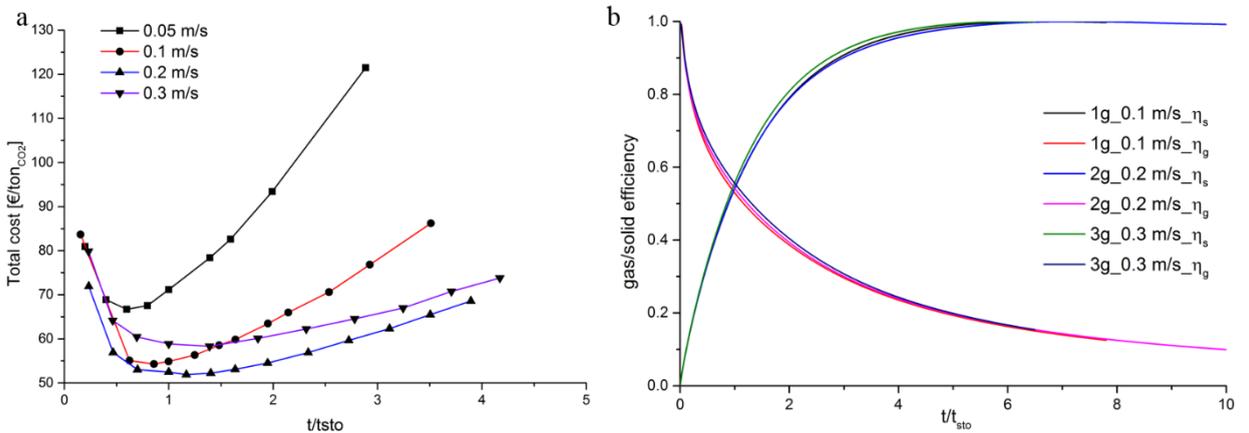


Fig. 5. (a) Total cost vs. adsorption time at other velocities ($p_{CO_2} = 40$ Pa, 298 K); (b) η_s and η_g vs. (t/t_{sto}) when $t_{sto} = \pm 43$ min

However, this optimal operating window of the velocity will most likely change somewhat for different bed lengths (different amount of sorbents). To translate the results found to different bed lengths, it seems appropriate to use t_{sto} for relating gas velocity (CO_2 supply) and bed length. The t_{sto} corresponding to $u_G = 0.1 - 0.3$ m/s at 1 g of IER used is between 14 min to 42 min. To test whether the stoichiometric time is a good measure for scale-up and for finding the optimum, experiments were conducted in the same reactor, now loaded with 2 and 3 g of IER. A value for $t_{sto} = 42$ min (related to the case of $u_G = 0.1$ m/s at a loading of 1 g of adsorbent) was maintained in experiments performed with 0.2 m/s with 2 g of sorbent and with 0.3 m/s with 3 g of sorbent. Fig. 5 (b) shows the comparison of the experimentally obtained solid / gas efficiencies with t/t_{sto} for these three different amounts of sample (covering a threefold increase in bed length). The results for the different bed lengths display great similarities in the development of their solid and gas efficiency with time, when operating at the same t_{sto} . Two conclusions can be drawn from the results. Firstly, external mass transfer does not have a significant influence on the uptake rate of the process, since operating at higher gas velocities results in similar performance. Secondly, the scaling technique based on the stoichiometric time is a useful concept for correlating experimental data, optimization studies and scale-up.

4.2. Reactor design

In the sections above, the feasibility of capturing CO₂ from air using a supported amine based sorbent in a fixed bed configuration was shown and a preliminary optimization study was done for finding the operating range for the optimum stoichiometric time and the adsorption time for an economic process. A low pressure drop during air-sorbent contacting is key for good economics of the process. Based on these considerations (low pressure drop and optimum stoichiometric time), a shallow bed of particles is required. To avoid extreme low ratios of contactor height/diameter, here a radial flow air-sorbent contacting method is selected as contactor for the adsorption step. In a radial flow reactor shown in Fig. 6 (a), the adsorbent is packed along the axial direction of the reactor and the gas flow passes through the bed of sorbents in radial direction (either inside-out or outside-in) and leaves the contactor at the same or opposite side of the contactor as where the feed enters. A radial flow is easy to scale up as it only needs to increase the length of the reactor instead of the diameter.

The main purpose of the radial flow reactor is to reduce the pressure drop in the adsorption and increase the adsorption performance. Based on the results in section 4.1, a polynomial relation between t_{sto} and its corresponding η_s and η_g when $t = t_{sto}$ has been established. This relation can be applied for sizing a lab-scale radial flow reactor. We proposed a scheme for calculating the dimensions of a lab-scale radial flow reactor. The assumptions of the calculation are listed as follows:

- For this calculation, the stoichiometric time was specified as 40 min and adsorption time was specified as equal to the stoichiometric time. This stoichiometric time is in the optimal range found in chapter 4.1.
- The cross-sectional area of central tube equals to the cross-sectional area of outer annulus.
- The combination of gas velocity and bed thickness should be realistic and feasible. In view of possible maldistribution a minimum bed thickness equal to 10-15x the particle diameter (say, 1.5 cm for the IER under consideration) seems appropriate.

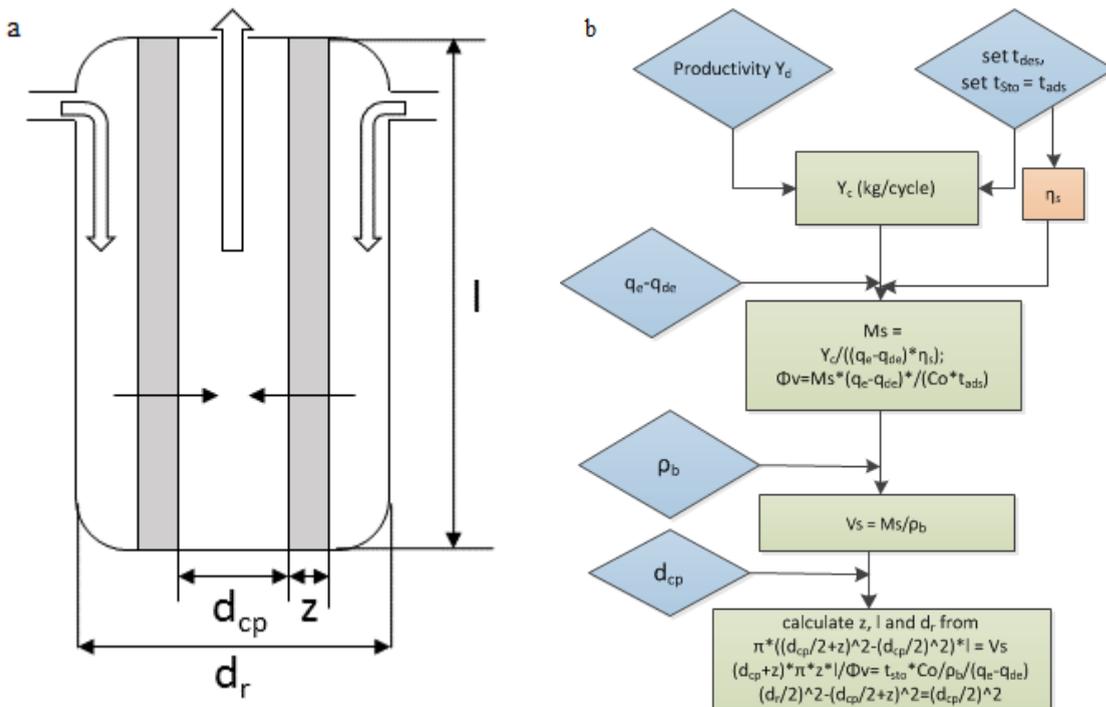


Fig. 6. (a) Schematic diagram of a radial flow reactor corresponding to the parameters in Table 2; (b) Calculation procedure for geometric dimensions of the radial flow reactor.

Taking into account above assumptions and the input parameters from Table 2, the procedure of the calculation is now shown in Fig. 6 (b). In Table 2 the results of the estimated reactor dimensions, required sorbent amount and the gas flow are listed for a daily productivity of 0.5 kg of CO₂. The pressure drop across the bed is calculated to be 140 Pa, according to the equation below

$$\frac{dP}{dr} = \left(\frac{150\mu(1-\varepsilon)^2}{\Phi_s^2 d_p^2 \varepsilon^3} \cdot \frac{\varphi_v}{2\pi L} \right) \frac{1}{r} + \left(\frac{1.75\rho(1-\varepsilon)}{\Phi_s d_p \varepsilon^3} \cdot \frac{\varphi_v^2}{(2\pi L)^2} \right) \frac{1}{r^2} \quad (14)$$

The integration of the radius is needed in this calculation, which is integrated from $r = 0.075$ m to $r = 0.09$ m according to the results shown in Table 2. The pressure drop of this proposed radial flow reactor is comparable with the pressure drop calculated in the Kulkarni and Sholl's study [12] to capture CO₂ from ambient air in a monolith reactor. The cost of the contacting energy and cost of sorbent are calculated to be 9.3 and 32.6 €/t_{CO₂}, using the parameters listed in Table 2.

Table 2. Reactor dimensions for 0.5 kg CO₂ per day.

Inputs	
Productivity Y_d (kg _{CO₂} /d)	0.5
Adsorption time t_{ads} (min)	40
Desorption time t_{de} (min)	60
Max. cyclic capacity ($q_e - q_{de}$) (g/kg _{IER})	44
Bulk density of the sorbent ρ_b (kg/m ³)	540
Diameter of the central annulus d_{cp} (m)	0.15
Outputs	
Sorbent efficiency η_s (-)	0.58
Cyclic yield Y_c (kg/cycle)	0.04
Amount of sorbent M_s (kg)	1.4
Air flow Φ_{air} (m ³ /h)	125
Volume of sorbent V_s (l)	2.5
Thickness of bed z (m)	0.015
Length of bed l (m)	0.32
Diameter of the reactor d_r (m)	0.24

5. Conclusion

Amine based sorbents can be used for atmospheric CO₂ capture in a fixed bed reactor. Due to the low concentration of CO₂ in air, sufficient CO₂ supply is an important parameter determining the kinetics of adsorption. Using the stoichiometric time concept, the CO₂ supply rate can be linked to bed length, gas removal fraction and sorbent efficiency. In this work, the stoichiometric time for CO₂ air capture and IER sorbent under consideration was tested to be at an economic optimum in the range of 15 – 45 minutes. The choice of adsorption time has a significant influence on process economics, resulting in an optimal operating window at $t_{ad} = 0.5 - 1.5 t_{sto}$. It was demonstrated here that when operating at the same stoichiometric time there was no influence in the uptake rate of CO₂ using different amount of sorbents (different bed lengths). A radial flow reactor was proposed and designed for further evaluation of CO₂ capture from ambient air.

Acknowledgement

This research was carried out within the EU MIRACLES project (www.miraclesproject.eu) and has received funding from the European Union's Seventh Framework Program for research; technological development and demonstration under grant agreement No 613588.

References

- [1] Raupach MR, Marland G, Ciais P, Quere CL, Canadell JG, Klepper G, et al. Global and regional drivers of accelerating CO₂ emissions. National Academy of Sciences of the USA 2007;104:10288-93.
- [2] IPCC. Climate Change 2007 Synthesis Report. 2007.
- [3] Lepaumier H, Picq D, Carrette P-L. New Amines for CO₂ Capture. II. Oxidative Degradation Mechanisms. Industrial & Engineering Chemistry Research 2009;48:9068-75.
- [4] Samanta A, Zhao A, Shimizu GKH, Sarkar P, Gupta R. Post-Combustion CO₂ Capture Using Solid Sorbents: A Review. Industrial & Engineering Chemistry Research 2012;51:1438-63.
- [5] Goto K, Yogo K, Higashii T. A review of efficiency penalty in a coal-fired power plant with post-combustion CO₂ capture. Applied Energy 2013;111:710-20.
- [6] Gebald C, Wurzbacher JA, Tingaut P, Zimmermann T, Steinfeld A. Amine-Based Nanofibrillated Cellulose As Adsorbent for CO₂ Capture from Air. Environmental Science & Technology 2011;45:9101-8.
- [7] Liu F-Q, Wang L, Huang Z-G, Li C-Q, Li W, Li R-X, et al. Amine-Tethered Adsorbents Based on Three-Dimensional Macroporous Silica for CO₂ Capture from Simulated Flue Gas and Air. ACS Applied Materials & Interfaces 2014;6:4371-81.
- [8] Lu W, Sculley JP, Yuan D, Krishna R, Zhou H-C. Carbon Dioxide Capture from Air Using Amine-Grafted Porous Polymer Networks. Journal of Physical Chemistry C 2013;117:4057-61.
- [9] Sculley JP, Zhou H-C. Enhancing Amine-Supported Materials for Ambient Air Capture. Angewandte Chemie-International Edition 2012;51:12660-1.
- [10] Brilman DWF, Veneman R. Capturing atmospheric CO₂ using supported amine sorbents. Energy Procedia 2013. p. 6070-8.
- [11] Veneman R, Frigka N, Zhao W, Li Z, Kersten S, Brilman W. Adsorption of H₂O and CO₂ on supported amine sorbents. International Journal of Greenhouse Gas Control 2015;41:268-75.
- [12] Kulkarni AR, Sholl DS. Analysis of Equilibrium-Based TSA Processes for Direct Capture of CO₂ from Air. Industrial & Engineering Chemistry Research 2012;51:8631-45.
- [13] Zhang W, Liu H, Sun C, Drage TC, Snape CE. Capturing CO₂ from ambient air using a polyethyleneimine–silica adsorbent in fluidized beds. Chemical Engineering Science 2014;116:306-16.
- [14] Smal IM, Yu Q, Veneman R, Fränzel-Luiten B, Brilman DWF. TG-FTIR Measurement of CO₂-H₂O co-adsorption for CO₂ air capture sorbent screening. Energy Procedia 2014;63:6834-41.
- [15] Gerhart Eigenberger WR. Catalytic Fixed-Bed Reactors. Ullmann's Encyclopedia of Industrial Chemistry 2012.
- [16] Werther J. Fluidized-Bed Reactors. Ullmann's Encyclopedia of Industrial Chemistry 2012.
- [17] Alesi WR, Kitchin JR. Evaluation of a Primary Amine-Functionalized Ion-Exchange Resin for CO₂ Capture. Industrial & Engineering Chemistry Research 2012;51:6907-15.
- [18] Sanz R, Calleja G, Arencibia A, Sanz-Pérez ES. CO₂ adsorption on branched polyethyleneimine-impregnated mesoporous silica SBA-15. Applied Surface Science 2010;256:5323-8.
- [19] Heydari-Gorji A, Sayari A. CO₂ capture on polyethyleneimine-impregnated hydrophobic mesoporous silica: Experimental and kinetic modeling. Chemical Engineering Journal 2011;173:72-9.
- [20] Choi S, Gray ML, Jones CW. Amine-tethered solid adsorbents coupling high adsorption capacity and regenerability for CO₂ capture from ambient air. ChemSusChem 2011;4:628-35.
- [21] Choi S, Drese JH, Eisenberger PM, Jones CW. Application of amine-tethered solid sorbents for direct CO₂ capture from the ambient air. Environmental Science and Technology 2011;45:2420-7.
- [22] Veneman R, Hilbers T, Brilman DWF, Kersten SRA. CO₂ capture in a continuous gas–solid trickle flow reactor. Chemical Engineering Journal 2016;289:191-202.
- [23] European Union Natural Gas Import Price. Commodity Markets Review Jun 2016.
- [24] Ray Sinnott GT. Chemical Engineering Design, 2nd Edition. 2012.