ECN-W--16-012

Separation and Purification Technology 184 (2017) 12–25

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

CO_2 removal from biogas with supported amine sorbents: First technical evaluation based on experimental data

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A R T I C L E I N F O

Article history:
Received 19 April 2017
Accepted 20 April 2017
Available online 23 April 2017

Keywords:
Biogas
CO_2 removal
Supported amine sorbents
Process evaluation

A B S T R A C T

Biogas from fermentation of manure and organic residues produces a gas stream that can be fed into the natural gas grid, provided impurities (CO_2, H_2S and H_2O) are removed according to specifications prior to grid injection. Compared to conventional technologies, supported amine sorbents (SAS) seem attractive for their high working capacity and fast uptake rate. In this study a technical evaluation for the conceptual design of a system for CO_2 capture from biogas with SAS is carried out and the performance is compared with liquid amine scrubbing. As the basis of this study, 1000 Nm^3/h of raw biogas with 45%-v of CO_2 is to be upgraded to gas product containing max. 10%-v of CO_2, according to low calorific gas specifications. For the selected SAS (Lewatit VP OC 1065 and PEI/SiO_2) capacity measurements were carried out and results were correlated by Toth sorption isotherms. The heat of adsorption was calculated from the isotherms using the Clausius-Clapeyron equation and validated by measurements at different temperatures using calorimetry. Using the isotherms, a process analysis study with Aspen Plus software was carried out to obtain the best operating conditions for temperature swing between adsorption and desorption conditions, and subsequently the contactor size was determined. System integration studies show that the heat released during the adsorption can be integrated with the heat required in the digester (~60 °C), resulting in a primary energy use of 20–22% for SAS, while for conventional amine scrubbing this is 38%. This study shows that SAS is an attractive technology option for CO_2 removal from biogas.

1. Introduction

Renewable biogas from anaerobic fermentation is an energy source that is receiving increasing interest. Biogas is formed via anaerobic fermentation of manure and organic residue streams in a digester. The raw biogas contains significant amounts of sour components such as CO_2 and H_2S. Before biogas can be utilized or injected in local gas grids, these contaminants must be removed from the gas stream to prevent corrosion and to increase the heating value of the gas. The removal of CO_2 is of primary interest, this being the primary constituent next to methane.

The market for biogas digester systems is young, fast growing and characterised by a large number of suppliers, each offering their own technology for gas upgrading. Several technologies compete on costs and performance. The main commercial technologies are water scrubbing, membranes, pressure swing adsorption (PSA), and chemical scrubbing using amines, according to an extensive overview [1]. These processes can be characterised on the basis of methane emissions, electricity use, heat use and waste produced, as presented in Table 1.

Membranes have a low thermal energy use, but require power for compression of feed and/or permeate gas. Limited selectivity of membranes towards CO_2 leads to methane being emitted along with the CO_2. This can largely be overcome using a line-up with two or more stages, but this comes with additional costs for permeate recompression. Water scrubbing has the advantage of being a relatively simple technology requiring heat to release the CO_2 from the water stream. Methane will, however, be co-absorbed in the water and released with the CO_2. PSA processes use mostly carbon-based sorbents at ambient temperature. The simplicity of

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Abbreviations: SAS, supported amine sorbents; PEI, polyethyleneimine; SiO_2, silicon oxide; SRPEU, system relative primary energy use; PSA, pressure swing adsorption; TGA, thermal gravimetric analyzer; DSC, differential scanning calorimetry; DTA, differential thermal analysis; SiC, silicon carbide; TSA, temperature swing adsorption; MEA, monoethanolamine; MDEA, methyldiethanolamine; L/R HX, lean/rich heat exchanger.

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http://dx.doi.org/10.1016/j.seppur.2017.04.030
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Table 1
Qualitative assessment of biogas processing technologies.

Technology	CH_4 emissions	Electricity use	Heat use	Consumables/waste
Membranes	–	O	–	+
Water scrubbing	–	O	+	–
PSA	–	–	+	+
Chemical scrubbing	+	O	–[a]	–
Supported amine Sorbents (SAS)[b]	+	+	O	+

[a] Use of rejected heat perhaps possible.
[b] Projected performance.

operation and high CO_2 partial pressure make (partial) PSA popular options. Compression power for running the pressure cycle is required, and co-adsorption of methane on the sorbent leads to significant methane losses and emissions. To avoid emissions of the methane, which is a much stronger greenhouse gas than CO_2, a more selective removal technology is desired.

Chemical solvent scrubbing using amines has the advantage of having a very high selectivity towards CO_2, as it is based on a specific chemical affinity for CO_2 and has no affinity to methane. In this way methane emissions can be minimized. Regeneration of the amine solution requires thermal energy. It is known that amines have a limited stability, so periodic replacement is required. Also metal corrosion is an issue frequently reported in amine systems [2].

The use of SAS to remove CO_2, H_2S and H_2O from sour, methane-rich gases (such as biogas and sour natural gas) as well as from flue gas (post-combustion CO_2 capture) is a relatively new development. In comparison with more conventional liquid phase processing, the application of these sorbents is attractive for different reasons: (i) It may reduce the energy requirement for sensible heat when switching between adsorption and desorption conditions, since the heat capacity of solids is lower than that of liquids and evaporation of water can be avoided [3]. (ii) It will potentially lower emissions of degradation products and minimize corrosion issues because of the immobilization of the amines. (iii) For small scale systems it may be easier to operate, if a simple gas-solid fixed bed can be used instead of a process with gas/liquid circulation. (iv) SAS can also be tuned thanks to the availability of various supports and active materials as discussed in several reviews [4,5]. The projected relative performance of SAS has been added to the overview in Table 1.

In the assessment of a novel technology, a design study provides the first insight of technical feasibility of the process. Hence in this paper, the design strategy for a supported amine-based adsorption system for CO_2 removal from biogas is discussed, using an integral approach addressing the interaction of sorbent characteristics, cycle design, heat management and system integration. Energy requirements and productivity of this process are compared with an amine-based solvent process as the most common technology for industrial CO_2 removal. A direct comparison between two technologies is not possible given the simplifications made in the SAS system and the higher uncertainty range for such a novel technology. Nevertheless, important insights in the potential and specific advantages and challenges of SAS technologies can be obtained. One specific potential advantage explored in this paper is that these sorbents can operate at relatively high temperatures and have a very large heat effect during adsorption because of the absence of evaporating water in the adsorber. This potentially allows heat integration with the fermenter.

2. Materials and methods

2.1. Materials

The first used sorbent is a commercial sorbent Lewatit VP OC 1065 from Lanxess. The sorbent has a support of spherical polystyrene beads with primary benzyl amine units [6]. Another sorbent is prepared in-house by impregnation of 35% w/w of polyethyleneimines (PEI), with a mixture of primary, secondary and tertiary amine groups and an average molar mass of 600 g/mol, on a silicon oxide (SiO_2) support. PEI based sorbents are chosen because they have been successfully utilized for CO_2 removal from air [7] or flue gas [8] in other studies.

2.2. Equipment

Capacities of the sorbents used at temperatures and partial pressures relevant to biogas upgrading were measured using Netszch STA 449 F1 Jupiter thermal gravimetric analyzer (TGA) with CO_2 concentration limited to 80%-v CO_2 at 1 atm. High purity (grade 5.0) N_2 and CO_2 gasses were used in the experiments. The procedure has been presented in a previous study [6].

The heat of adsorption is measured calorimetrically using a Mettler-Toledo TGA-DSC1 (Differential Scanning Calorimetry) with DTA (Differential Thermal Analysis) sensor, following a similar procedure as described in the previous section. For a certain amount of sorbent, the total quantity of heat produced during the adsorption process is obtained by integrating the calibrated sensor output (voltage over time), which can be recalculated to the heat of adsorption in J/mol CO_2.

Adsorption studies on ternary mixtures with all the major components found in biogas (CH_4, CO_2, H_2O, H_2S) were carried out in a packed bed reactor with 2.5 g PEI/SiO_2 (PEI/SiO_2:Silicon Carbide (SiC) = 1:11; inertness of SiC verified) at 40 °C (and a limited set of experiments at 60 °C), desorption at 110 °C, 80 mL/min in atmospheric pressure. The adsorbent was first pre-conditioned in 5% H_2O-N_2 at 110 °C. It was then exposed to the gaseous mixture fed for the selected experiment at 40 °C for 30 min. The temperature was then increased to 110 °C in N_2 with 5%-v H_2O for 30 min of regeneration. The sorbent was then cooled down in dry N_2 to the adsorption conditions. Each setting was repeated for 5 cycles and all reported capacities are breakthrough capacities.

2.3. System modeling

2.3.1. Digester

The formation of biogas in the digester is not considered in detail, but the heat demand that is relevant for system integration is taken into account in the model. Methane production by anaerobic digestion can be done at different temperature levels. Mesophilic digesters operate at 35–40 °C and are generally robust [9]. Thermophilic digesters operate at a somewhat higher temperature level of 45–55 °C, are less stable, but can achieve a higher throughput. Larger scale systems are generally fed with relatively stable feed streams, and thermophilic digesters are preferred because of their higher throughput. These digesters are generally well insulated, and heating of the feed streams is a main requirement. Heating is generally done through the walls or floor of the digester and a temperature difference with the heating medium of 5–10 °C is sufficient. In the digester itself, heat is also generated depending on the energy content of the digester feed. Thus, the net amount of heat that needs to be supplied to the digester can vary in the range of 0–25% of the LHV output and a representative heat demand of 15% has been selected, which need to be supplied at 60 °C including the temperature difference for heat transfer [10–13]. The biogas composition used in this study is shown in Table 2.

2.3.2. Biogas upgrading

In the upgrading process, the raw biogas product from the digester is processed to meet the requirements of the natural gas grid. For the current study, the low-calorific-medium-pressure natural gas is selected. Specifications are summarized in Table 3 [14]. In order to meet these specifications, specifically H_2S, CO_2, and H_2O need to be removed, and the pressure needs to be increased.

Given that the biogas is produced at atmospheric pressure and that approximately one third of the gas volume is to be removed in the process (from 45%-v to 10%-v), compression of the total biogas feed would require more energy than compressing the product gas. On the other hand, boosting the pressure prior to CO_2 removal would increase the partial pressure of CO_2, leading to smaller adsorption equipment. However, compared to the high gas flow rates and high pressures present in natural gas treatment, the decrease in absolute size and associated costs are quite small for these relatively small gas flow rates and low pressures, decreasing the potential benefit of feed gas compression. Hence, operating the adsorber at atmospheric pressure and increasing the pressure of the cleaned gas stream afterwards is more attractive.

Sulphur scavenging by iron sponge (dry iron oxide) is selected for removing traces of H_2S because of its ability to selectively capture hydrogen sulphide (in presence of carbon dioxide) and the ease of operation [15]. After desulphurisation, the carbon dioxide is removed by the supported amine system, the selection of which is further discussed in Section 2.5. This led to the selection of the fixed bed contactor for CO_2 removal, with a temperature swing adsorption (TSA) as regeneration method. In order to achieve a high thermal efficiency, opportunities for heat integration are explored. The general flowsheet is depicted in Fig. 1. The SAS system requires high-temperature heat which is supplied by the central boiler system (Fig. 1). Rejected heat from the SAS is used to provide heat to the digester.

Once the sour components are removed, the gas is cooled and water is potentially condensed before the final drying step in the desiccant adsorption column (Fig. 1G), which is required to achieve the dew-point product specification. The desiccant (molecular sieves, silica gel or $Na_2O\text{-}SiO_2$) is regenerated by heating part of the processed gas to 250 °C, as purge gas [16]. The overhead vapor is recycled to recover the product.

$$SRPEU = \frac{\phi_{internal} \cdot LHV_{internal} + P_{tot}/\eta_{power}}{\phi_{raw\_gross} \cdot LHV_{raw\_gross}} * 100\% [\%] \quad (1)$$

Equation 1. Definition of System Relative Primary Energy Use (SRPEU).

For the system simulations, the energy use in the biogas upgrading process is reported as the System Relative Primary Energy Use (SRPEU), as defined in Eq. (1). This gives the relative amount of feed gas consumed in the processing, expressed in terms of primary energy, combining the heat use and electricity use. Hence, SRPEU represents the amount of cleaned gas used internally for the boiler ($\phi_{internal}$) to match the internal heat demand, plus the total power use (P_{tot}) converted to primary energy using the conversion factor (η_{power}) of 43.6% [17]. It is chosen here to divide by the gross production of raw biogas (ϕ_{raw_gross}), to correct for potential methane loss in the different technologies. Cooling duty that can be removed by air-cooled coolers is not taken into account in the SRPEU, as the energy needed for the fans is negligible in comparison to the cooling duty.

Table 2
Biogas from anaerobic thermophilic fermentation.

Temperature	20	°C
Pressure	1.023	Bar (a)
Flow rate	1000	$Nm^3 h^{-1}$
Composition		
CH_4 (balance)	54.3	%-v (dry)
CO_2	45	%-v (dry)
N_2	0	%-v (dry)
H_2S	0.5	%-v (dry)
O_2	0.2	%-v (dry)
H_2O	100	% relative humidity

Table 3
Product specification derived from the natural gas grid [14].

Specification	Value	Unit	Comment
Pressure	8	bar	Medium pressure grid
Composition			
CO_2	$\leq$10	%-v	
H_2S	<3.5	ppm-v	
Dew point	−10	°C	
Wobbe index	43.46–44.41	MJ/Nm^3	

2.4. Design and modeling approach of SAS CO_2 capture unit

2.4.1. Reactor concept selection

For removal of CO_2, selection of reactor type and regeneration strategies are the most important aspects in the design process. Depending on the nature of the gas stream, the CO_2 concentration and water content, the most optimal contactor and process may vary. For near-atmospheric pressure systems (as in biogas systems), pressure drop can be a leading design criterion. However, also the CO_2 content is relevant, and the application of sorbents with low heat capacity could lead to a high temperature increase in the adsorption step, making the heat removal strategy an important issue. Additionally the operational simplicity and investment costs are important, as stated in Section 2.3.2.

For the SAS system two basic gas-solid contactor types are possible; with- and without solids circulation. The first option employs solids circulation in a circulating fluidized bed assembly, consisting of a multi-stage or trickle flow adsorber, and a regenerator which is a bubbling fluidized bed using a CO_2/H_2O product recycle for fluidization [18]. Here the adsorber concept is aimed at optimal productivity and counter-current contact between sorbent and gas during adsorption. The solids are transported from one reactor to the other by gravity, by a transport gas or screw conveyors.

The second option envisaged, without solids circulation, is a fixed bed adsorption system with a temperature swing as regeneration. Assuming a two bed system, one bed is in adsorption mode, whereas the other is being regenerated. Once the adsorption bed is fully loaded with CO_2, a valve system switches the operating modes of the two beds. The adsorption step starts with bed filled with sorbent that is regenerated until CO_2 lean conditions, so that the CO_2 from the feed gas will be adsorbed until the gas phase CO_2 partial pressure is in equilibrium with the sorbent loading under lean conditions. Because of the higher level of operational simplicity and the expected lower investment costs, the fixed bed option was selected. Likely a rinse step is required in between adsorption and regeneration mode.

For both envisaged CO_2 removal systems, there is a considerable heat demand in the regenerator and heat release in the adsorber.

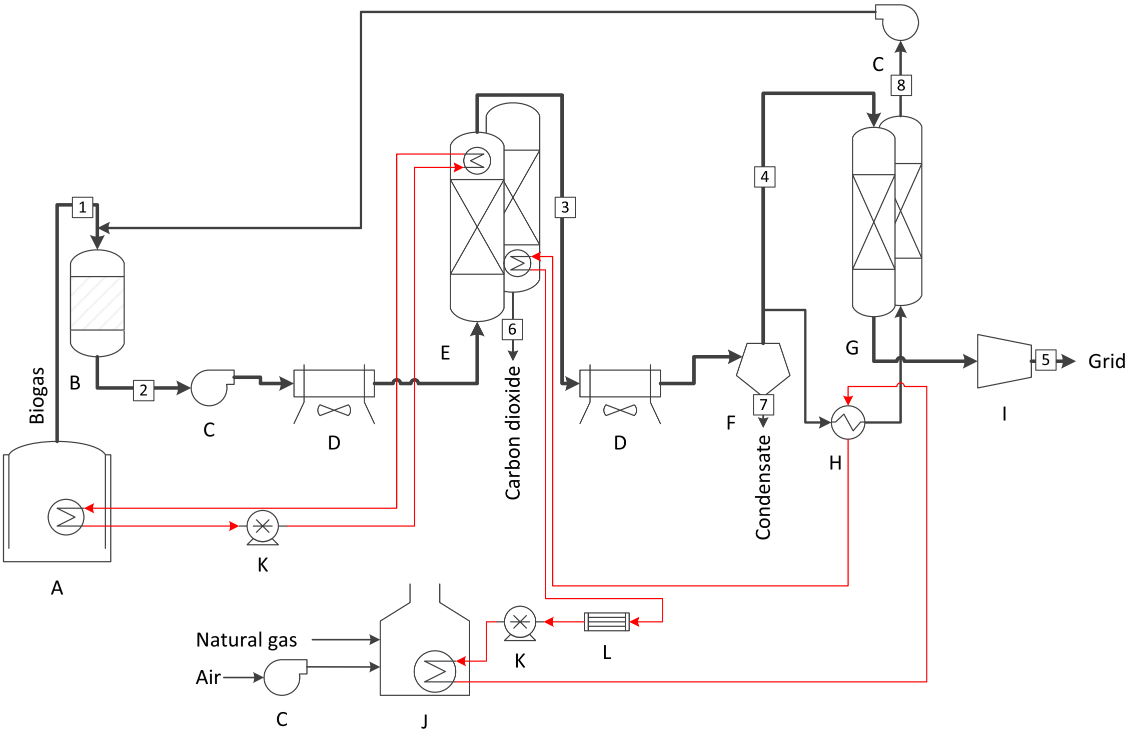

Fig. 1. Biomass upgrading flowsheet; A. Digester, B. H_2S scavenger, C. Fan, D. Air cooler, E. SAS unit, F. Knockout vessel, G. Desiccant column, H. Heat exchanger, I. Compressor, J. Boiler, K. Pump, L. Condenser.

Hence, both the fluidized beds as well as the fixed bed assembly require integration of heat exchange area for heat transfer to a thermal fluid (e.g. water or thermal oil) to integrate this heat in the process. For the model it is assumed that the heat transfer requirements can be fulfilled and that the solids and gas streams have a uniform temperature with full equilibration of temperatures between gas and solid at the exit.

2.4.2. SAS unit and system model

To allow for a flexible evaluation of the relation between sorbent characteristics and SAS system performance, a simplified model was constructed. From thermogravimetric analysis, adsorption kinetics proved to be very fast (seconds) and the process design was therefore assumed to be governed by equilibrium capacities, rather than on adsorption kinetics and mass transfer limitations. With this assumption, a sorbent based CO_2 removal unit has been modeled in a flow sheeting tool (Aspen Plus V8.4 [19]), which solves the mass and heat balance making use of the measured sorption isotherms. The system is depicted in Fig. 2 as a continuous process but could in principle represent either the fluidized bed or the fixed bed system.

The starting point for the model is the assumption for temperature equilibration for CO_2 between gas phase and solids at the outlets and adsorption equilibria between the sorbents and the gas phases at both inlet and outlet of the adsorber. For the adsorber this is based on a counter-current flow between sorbent and gas in the adsorber, achieved e.g. by selecting a fixed bed approach or a trickle bed adsorber or multi-stage fluidized bed contactor. The CO_2 loading of the rich sorbent is in equilibrium with the feed composition of the bio gas stream, and the cleaned product gas stream is assumed at equilibrium with the lean sorbent stream. The regenerator is modeled with gas and solids in cross-flow configuration, assuming equilibrium between the gas and solid outlet streams. This is, as a first approach, in accordance with the regenerator concept consisting of a well-mixed bubbling fluidized bed, using a CO_2/H_2O product recycle for fluidization.

For the fixed bed contactor option, the model represents also a temperature swing cycle in which two beds are used in alternating mode for adsorption and regeneration. Because of the counter-current operation and fast kinetics, the CO_2 loading of the rich sorbent is equal to the equilibrium loading of the sorbent at the feed gas partial pressure of CO_2. For the regenerator an equilibrium between product gas and end-of-cycle loading is assumed.

For water sorption in the adsorber, the model calculates the amount of water that can be adsorbed from the feed gas, given the feed and product gas partial pressures (similar to what is done for the CO_2 isotherms). Next to this, it takes into account that the amount of water available might not be sufficient for full loading of the sorbent, for which the model then limits the water uptake to the maximum possible.

Input to the model are the feed gas specifications, product gas specifications, adsorber operating conditions (temperature and pressure), and the sorption isotherms for both CO_2 and water. Main output from the model is the heat demand for regeneration and the required regeneration temperature. The required regeneration temperature is calculated by iterating until the regenerated sorbent is sufficiently lean to achieve the target fraction CO_2 in the product gas. The model calculates and reports the composition and flow rates of all streams. The amount of CO_2 in the clean gas here is thus determined by iterating over the regenerator temperature, which is the main parameter determining the lean loading of the sorbent. The amount of sorbent circulating is taken as the minimum value (through iteration), necessary to exactly load the sorbent to equilibrium loading at the feed gas conditions.

Parameters to the model are the constants in the Toth isotherms for CO_2 and a linear description of water sorption capacity using a Henry isotherm. Both for CO_2 and water the heat of sorption is considered in the calculations. The heat effect of CO_2 proved however to be dominant over that of water hence the results discussion will focus on CO_2 sorption. The heat of adsorption for CO_2 is sorbent loading dependent, and in the simulations the average heat effect for lean and rich conditions has been used.

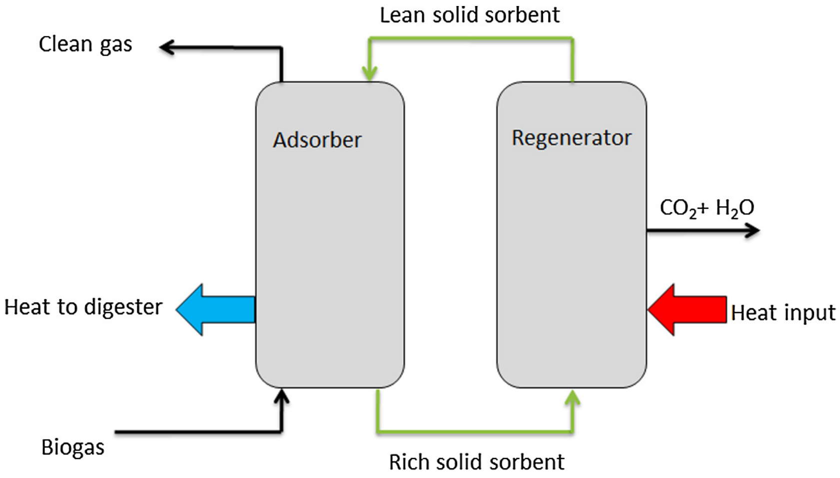

Fig. 2. Schematic process model for a SAS unit for CO_2 removal from biogas.

To allow for a flexible evaluation of the many design variables in this stage of the conceptual process evaluation, some important simplifications underlie the current approach. For fixed bed systems this includes ignoring the use of rinsing gas and not taking into account the ultimate fate of interstitial gas (e.g. loss of methane). Also the sensible heat involved with heating part of the reactor wall and heat transfer medium is not included. For a fluidized bed system, all streams and energy related to fluidization is excluded. These aspects are related to sizing of the equipment, as well as detailed cycle design and optimization. While these aspects certainly need to be accounted for in future developments, the current analysis is a valid approach to establish the potential of SAS technology for biogas upgrading.

The volumetric productivity is a measure for the size of the system, using the sizing of the main dimensions of a fixed bed adsorption unit respectively amine adsorber. The productivity is defined as the specific molar rate of CO_2 removal (mol/s) per unit of total CO_2 removal unit volume. For the sorbent unit this assumes 300 s cycle time, sorbent density of 1400 kg/m^3, sorbent porosity of 0.5, bed porosity 0.5, 30% of the reactor volume occupied by heat exchange tubes and three reactors operating in parallel.

The SAS system model has been built in Aspen Plus V8.4, using Redlich-Kong-Soave equation of state with Boston-Mathias modifications. ASME 1967 steam table correlations were used in the design of the steam system.

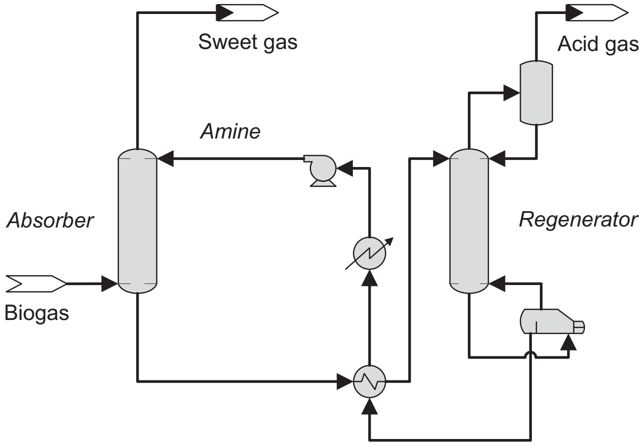

Fig. 3. Flowsheet for liquid amine scrubbing.

2.5. Amine scrubber design approach

The amine scrubbing process (Fig. 3) was simulated in a gas treating-specific simulation program (Protreat v5.5) and uses monoethanolamine (MEA, 27%-w) with minimized flow and reboiler duty. As the assumed incentive of SAS is increased energy efficiency, the amine design focused on getting the least energy consumption that would still be realistic and give stable operation. A methyldiethanolamine (MDEA) system has also been designed but proved less competitive than MEA. A more detailed explanation on the assumption is given in Appendix A. For liquid amine scrubbing the productivity is calculated based on the total volume of column packing required.

3. Results and discussion

3.1. Experimental results

3.1.1. Adsorption capacity

TGA provides measurements of the equilibrium adsorption capacities at different temperatures and CO_2 partial pressures. Fig. 4 includes literature data for the same Lewatit sorbent [6] and extends the range of process conditions related to those of biogas treatment (45% CO_2 at 1 atm). Fig. 5 presents similar results in the form of Toth isotherms for PEI/SiO_2 sorbent. The standard deviations of the measurements are 4.7% and 10.4% for Lewatit and PEI/SiO_2, respectively based on duplo experiments.

For Lewatit, the highest CO_2 capacity (2.95 mol/kg) is obtained at the lowest temperature studied (30 °C) and the highest CO_2 partial pressure applied (0.8 bar), which is expected for an amine-based sorbent. From an elemental analysis experiment of the sorbent, a nitrogen content of 8.5%-w is found, which would translate to a maximum CO_2 loading of 3.05 mol/kg assuming and Amine: CO_2 reaction stoichiometry of 2:1, in line with a carbamate formation mechanism. This result seems to be in line with that of actual TGA data for CO_2 adsorption, with a 97% utilization of the amine functionalities in the adsorption experiments.

For PEI/SiO_2 sorbent an anomaly was observed for temperatures between 40 and 80 °C, where the CO_2 adsorption capacity is increasing instead of decreasing with temperature. A similar observation was also found in previous study by Drage et al. [20]. A possible explanation for this may be found in the change of viscosity of PEI with temperature, unlocking initially inaccessible CO_2 sorption capacity at elevated temperature. Alternatively, the substituents

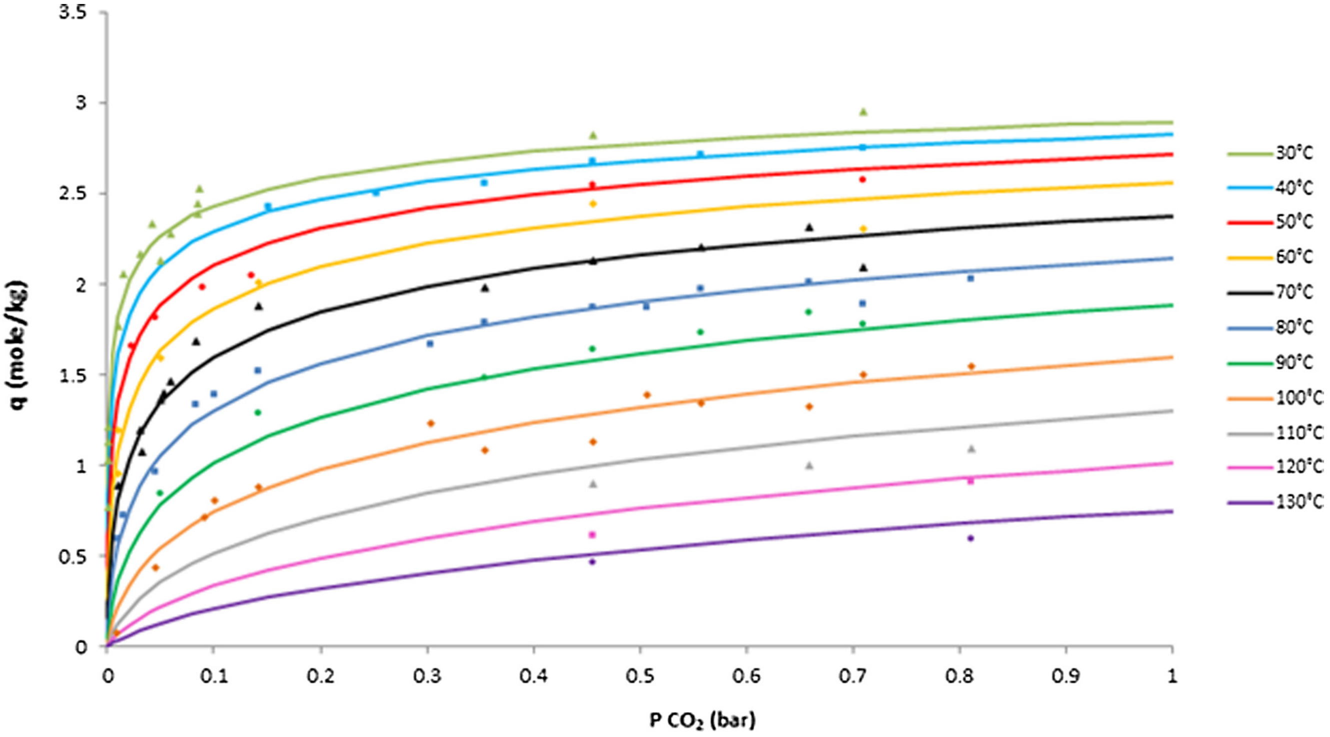

Fig. 4. Adsorption isotherms data for Lewatit VP OC 1065 sorbent at 30–130 °C and partial pressure of 0–0.8 bar CO_2. The points represent the experimental data and the lines represent the isotherm fit.

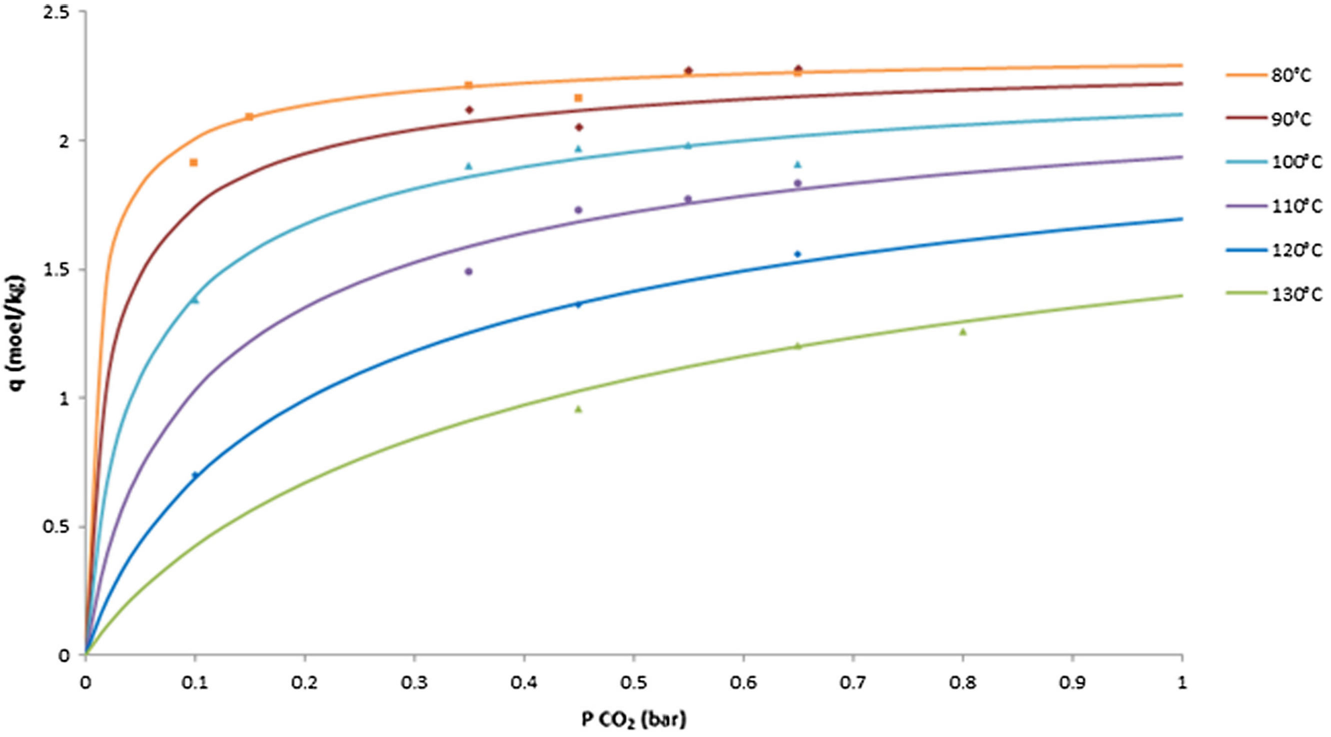

Fig. 5. Adsorption isotherms data for PEI/SiO_2 sorbent at 80–130 °C and partial pressure of 0.1–0.8 bar CO_2. The points represent the experimental data and the lines represent the isotherm fit.

on the amine could be of influence, but the observed behavior was not investigated further in detail. For further analysis only the capacities at temperatures between 80 and 130 °C were used.

As such, for PEI/SiO_2 sorbent the highest CO_2 loading of 2.26 mol/kg is obtained at 80 °C and 0.65 bar. From elemental analysis experiment, the percentage of nitrogen element content is

Table 4
Resulting Toth isotherm parameters.

Toth parameters	Lewatit	PEI/SiO$_2$
b_0 (bar^{-1})	188.6	71.9
t_0	0.3	0.7
n_{s0} (mol/kg)	3.7	2.4
ΔH^* (kJ/mol)	111.2	98.1
α	0.5	−0.1
T_0 (K)	353.2	353.2
χ	0	0

Table 6
Breakthrough capacities of simulated biogas at 40 and 60 °C.

Component	Biogas uptake by PEI/SiO$_2$ (mol/kg)		Biogas uptake by Lewatit (mol/kg)	
	40 °C	60 °C	40 °C	60 °C
CH_4	0	0	0	0
CO_2	1.39	1.3	0.94	0.75
H_2S	0.0165	0.0125	0.0089	0.005
H_2O	0	0.18	0.13	0.54

9.8%-w which translates to a maximum loading of 3.5 mol/kg. This result shows a 65% utilization of the amine functionalities, indicating that there are free active sites on the sorbent at the measured process conditions.

As in previous work with Lewatit sorbent, a Toth isotherm (Eq. (2)) has been adopted in this study [6]. The Toth isotherm formulated as follow [21]:

$$\begin{aligned} q &= \frac{n_s \cdot b \cdot P}{\left(1+(b\cdot P)^t\right)^{\frac{1}{t}}} \\ b &= b_0 \cdot \exp\left[\frac{\Delta H}{R\cdot T_0}\left(\frac{T_0}{T}-1\right)\right] \\ t &= t_0 + \alpha\left(1-\frac{T_0}{T}\right) \\ n_s &= n_{s0}\cdot exp\left[\chi\left(1-\frac{T}{T_0}\right)\right] \end{aligned} \tag{2}$$

Equation 2. Toth isotherm and its temperature-dependent terms (parameters in Table 4).

Based on the extended data in Figs. 4 and 5, the calculated parameter values (see Table 4) were determined by using the least square method to Toth isotherm for both Lewatit and for PEI/SiO$_2$ sorbent. For PEI/SiO$_2$ sorbent, only the data above 80 °C is used to estimate the parameters.

Sulphur scavenging by iron sponge (dry iron oxide) was selected in the process scheme shown in Fig. 1 to selectively capture hydrogen sulphide. However, in the event of a malfunctioning or general process interruption, H_2S may slip through to the SAS CO_2 capture unit, and in that scenario the SAS sorption capacity for CO_2 should not be compromised. Adsorption studies on the ternary mixtures in a fixed bed with 1 atm feed of 45.4% CH_4, 37.1% CO_2, 0.5% H_2S, 7% H_2O and balance N_2 are shown in Table 5. The results indicate that the CO_2 breakthrough capacity appeared to remain quite stable for PEI/SiO$_2$ and decreased somewhat for Lewatit. The breakthrough of H_2O considered here did not take into account the slip level (less than 5% of the initial concentration).

Simulated biogas mixtures experiments were carried out with a feed gas containing 4000 ppm H_2S, 5.7% H_2O, 30% CO_2, 36.3% CH_4, 13.3% N_2 and 14.3% He (biogas composition from Table 2, diluted with He because of experimental limitations), the results are shown in Table 6. The adsorption temperature was varied at 40 and 60 °C. For PEI/SiO$_2$ and Lewatit, the CO_2 breakthrough capacity appear to remain quite stable. The water uptake as well as the H_2S uptake seem to decrease with temperature. The interaction between all major components in the biogas does not affect the CO_2 breakthrough capacity (the amount of CO_2 removed by a certain amount of SAS at break point concentration).

3.1.2. Heat of reaction

The heat of reaction determines the change of temperature of the system during the exothermic adsorption step and the endothermic desorption step. It represents the amount of energy required to regenerate the sorbent and is thus a key parameter in CO_2 capture. The CO_2 isotherm is used to calculate heat of adsorption at different temperature and loadings via the well-known Clausius-Clapeyron equation in Eq. (3). The results are presented in Figs. 6 and 7. The experimental values from dedicated TGA-DSC experiment are also presented in these figures.

$$\mathrm{Ln}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \tag{3}$$

Equation 3. Clausius-Clapeyron equation.

It was reported that applying Clausius-Clapeyron equation to calculate the isosteric heat of adsorption requires two conditions: ideal gas phase behavior and negligible adsorbed phase volume. These approximations are not valid at high pressures or when the loading is above 3 mol/kg [22]. However, since the anticipated operating conditions are below these values, we have applied the ΔH calculation using Clausius-Clapeyron approach in our case. Two temperatures are fixed and at a certain loading and the corresponding partial pressure are calculated by using the isotherm. These data are then used to calculate the heat of adsorption by using the Clausius-Clapeyron equation.

The heat of adsorption at zero loading ($\Delta H*$) is taken from the isotherm (Table 4). The isosteric heat of adsorption at zero loading for primary amine is almost similar in value (111 kJ/mol) with that from literature [2]. As shown in Fig. 6, the isosteric heat of adsorption declines with the increase of loading, which is also in line with previous study [2].

For Lewatit, the heat of adsorption is measured at 70, 80 and 100 °C at a CO_2 concentration of 50%-v at 1 atm which leads to values of 66.5, 88.5 and 79.3 kJ/mol, respectively. For PEI/SiO$_2$ sorbent, the heat of adsorption calculated from Clausius-Clapeyron as well as the measured values in TGA-DSC of 100 kJ/mol seem independent of the loading and temperature (see Fig. 7). The mechanism behind this is not clear. It seems that the Clausius-Clapeyron approach applied to the experimental determined isotherms can

Table 5
Breakthrough adsorption capacity of ternary mixtures at 40 °C.

Component	Ternary mixture uptake by PEI/SiO$_2$ (mol/kg)		Ternary mixture uptake by Lewatit (mol/kg)	
	$CH_4/CO_2/H_2O$	$CH_4/CO_2/H_2S$	$CH_4/CO_2/H_2O$	$CH_4/CO_2/H_2S$
CH_4	0	0	0	0
CO_2	1.36	1.34	0.95	0.7
H_2S	0	0.0165	0	0.01
H_2O	>1.3	0	0.72	0
N_2	0	0	0	0

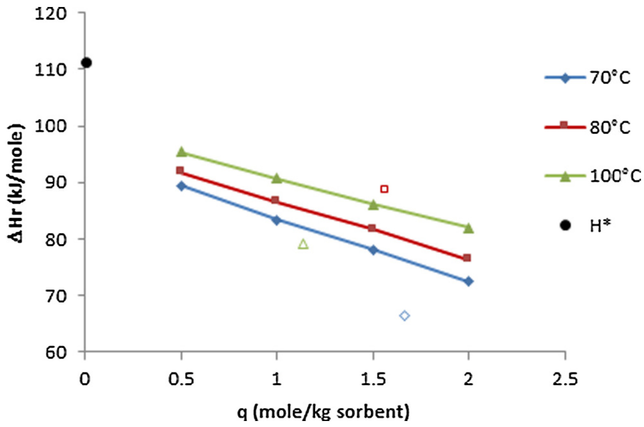

Fig. 6. Heat of adsorption of Lewatit at different loading. The open symbols are the experimental data and the full symbols are calculated using Clausius-Clayperon. The lines are given as guidelines.

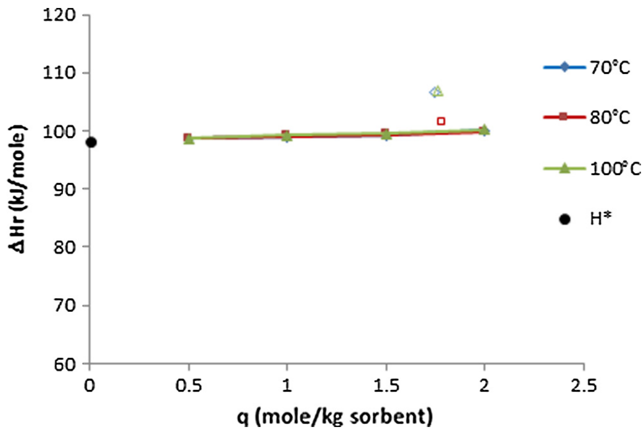

Fig. 7. Heat of adsorption of PEI/SiO$_2$ at different loading. The open symbols are the experimental data and the full symbols are calculated using Clausius-Clayperon. The lines are given as guidelines.

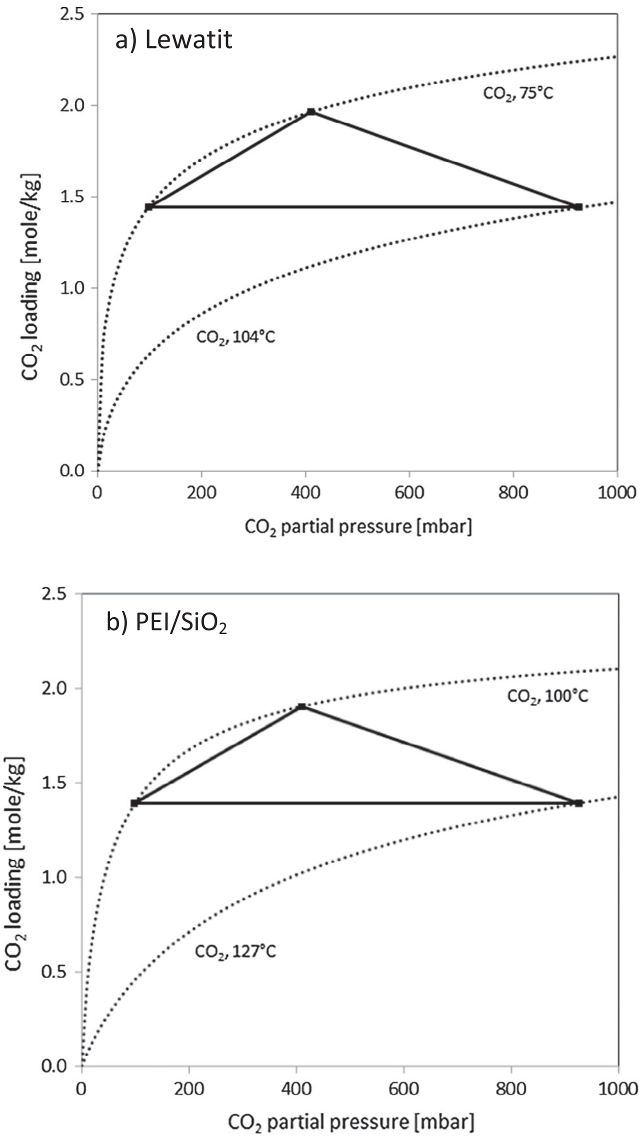

Fig. 8. Adsorption-desorption cycle for Lewatit (a) and PEI/SiO$_2$ (b) depicted on the isotherm graph. Solid line connects regenerator outlet, adsorber lean-end and adsorber rich-end conditions. Dashed line presents the isotherms at adsorber and desorber temperature.

predict the experimental determined heat of adsorption relatively well for PEI/SiO$_2$ while there is 5–10 kJ/mol difference for Lewatit.

3.2. Simulation of SAS unit operation

3.2.1. Basic cycle design

Using the isotherms from Figs. 4 and 5 it is possible to design a cyclic adsorption-desorption process for either sorbent. Fig. 8 depicts an example of such a design cycle. Combining the temperatures and loadings from the cycle design the energy balance of the cycle was calculated, based on adsorption enthalpy of water and CO$_2$ and the sensible heat involved in heating and cooling.

3.2.2. Cycle design optimization

From the cycle design and the resulting energy consumption, it becomes clear that the cyclic capacity is more important than the absolute capacity, and as such the energy consumption of the process depends very much on the selected temperatures. The main design variable in the cycle design is the adsorber temperature. Given this temperature, the regenerator temperature and cyclic capacity follow from the required CO$_2$ specification of the product gas.

At a low adsorption temperature the absolute capacity is high, so the rich loading of the sorbent is high (which increases adsorption enthalpy) but lean sorbent need not be that lean. Alternatively, at higher adsorption temperatures the capacity is lower, but sorbent should be much leaner (requiring deeper regeneration). This interdependency is summarized in Fig. 9, which shows a sensitivity study on the adsorber temperature in which a design variable can be chosen freely. Please note that for PEI/SiO$_2$ the isotherm is extrapolated below the temperature range used for fitting the isotherms. The required regeneration temperature (straight lines) is iterated with the model until the CO$_2$ concentration of the clean biogas achieves the specified value of 10% (see Section 2.4.2). The higher the regenerator temperature, the leaner the sorbent. Since equilibrium between lean sorbent and clean biogas is assumed, this determines the clean biogas conditions. The results show that the regeneration temperature increases with increasing adsorber temperature because the sorbent has to be leaner in order to remove up to 10% CO$_2$ in the clean biogas. With varying the adsorber temperature and regenerator temperature, the lean and rich loading will vary and thus the cyclic capacity (the difference

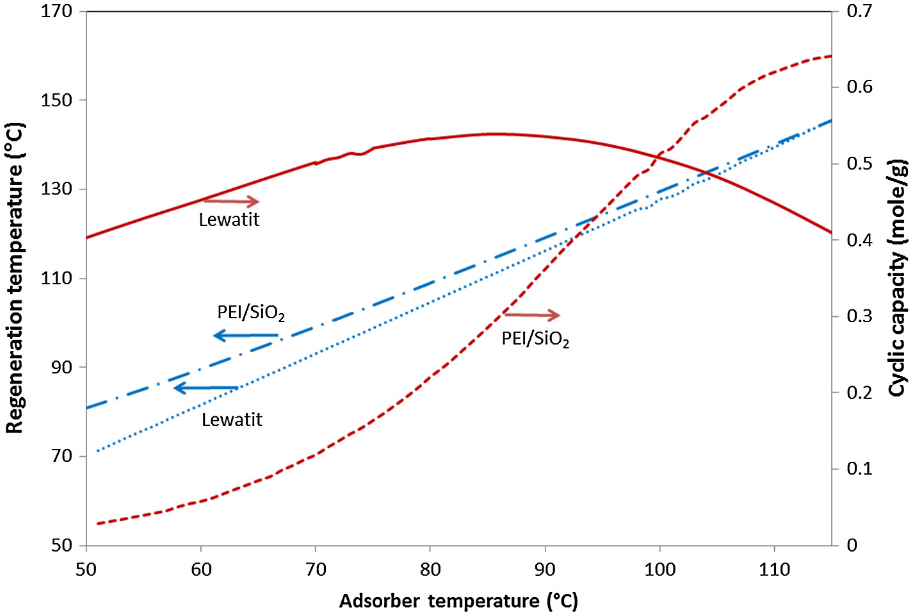

Fig. 9. Impact of adsorber temperature on regeneration temperature and cyclic CO_2 capacity.

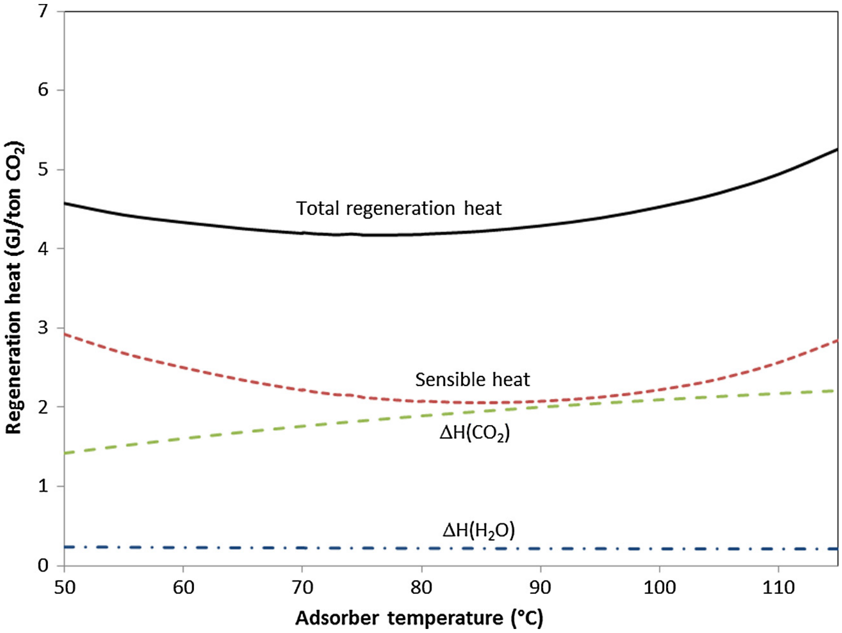

Fig. 10. Impact of adsorber temperature on regeneration heat for Lewatit.

between lean and rich loading) will also vary. The result in red line[1] show the complex interaction between lean loading and rich loading with adsorber temperature.

The model gives the regeneration heat as an output, as well as a breakdown of its three main contributions: (i) the heat for CO_2 desorption, (ii) the heat for water desorption, and (iii) the sensible heat to heat the sorbent mass from adsorption to regeneration conditions. The regeneration heat and its breakdown into individual contributions is provided in Figs. 10 and 11, for Lewatit and PEI/SiO_2 sorbent, respectively. The contribution of the heat of adsorption for CO_2 and the sensible heat for heating the sorbent from adsorption to regeneration conditions is of equal importance. The heat for water desorption is only a minor contribution. It can be seen that a minimum in the regeneration heat is found for Lewatit at an adsorber temperature of 75 °C. The resulting regenerator temperature is 104 °C. This is chosen as the design point to minimize the amount of heat transfer required in the process. For PEI/SiO_2 sorbent the energy minimum is 130 °C, the approximate limit above which stability issues with the sorbent are expected. Hence for PEI/SiO_2 an adsorber temperature of 100 °C has been selected, which limits the regeneration temperature to 127 °C.

3.2.3. Selected designs SAS

Table 7 gives a summary of the advised working conditions and performance of the SAS for fixed bed operation. Note that the work

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[1] For interpretation of color in Fig. 9, the reader is referred to the web version of this article.

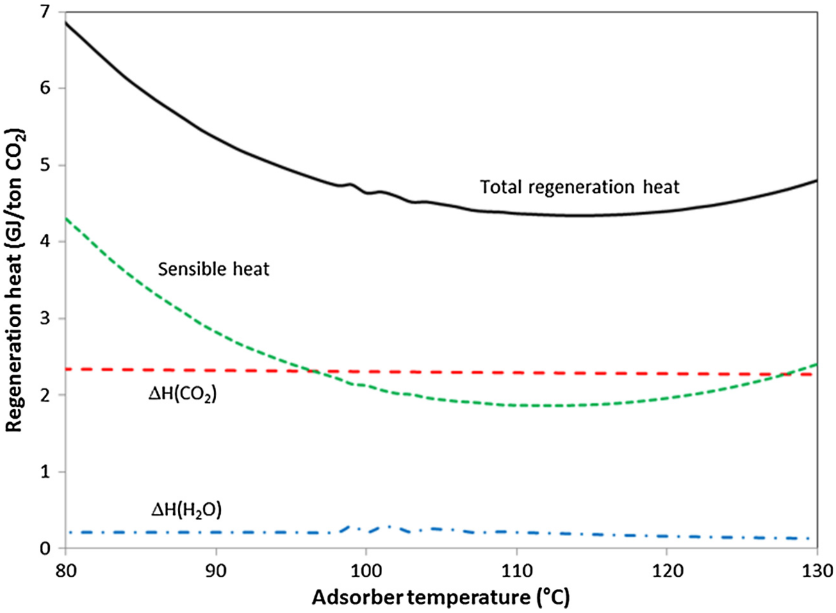

Fig. 11. Impact of adsorber temperature on regeneration heat for PEI/SiO_2.

Table 7
Aspen simulation results for SAS unit operation.

Parameters	Lewatit	PEI/SiO_2
Adsorber temperature	75 °C	100 °C
Regenerator heat demand (GJ/ton)	4.2	4.6
Adsorber heat released (GJ/ton)	4.0	4.4
Regenerator temperature	104 °C	127 °C
Cyclic capacity (mol/kg)	0.52	0.51
Feed gas	41.5% CO_2, 2.8% Water	41.5% CO_2, 2.8% Water
Lean sorbent (after regenerator)	1.15 mol CO_2/kg, 0.38 mol H_2O/kg, 104 °C	1.39 mol CO_2/kg, 0.09 mol H_2O/kg, 127 °C
Rich sorbent (after adsorber)	1.69 mol CO_2/kg, 0.42 mol H_2O/kg, 75 °C	1.91 mol CO_2/kg, 0.14 mol H_2O/kg, 100 °C
Clean gas	9.8% CO_2, 2% H_2O	9.8% CO_2, 2% H_2O
CO_2 product	90.9% CO_2, 9.1 H_2O	90.9% CO_2, 9.1% H_2O

Table 8
Stream table for biogas upgrading system with SAS.

	From	To	T (°C)	P (bar)	Flow rate (kmol/h)	Concentration (%mol)				
						CH_4	CO_2	H_2S	O_2	H_2O
1	Digester	H_2S scavenger	20	1	44.6	53.4	44.3	0.5	0.2	1.6
2	H_2S scavenger	Fan	48	1	48.4	55.6	41.5		0.2	2.8
3	CO_2 adsorber	Air cooler	40	1.2	30.6	87.9	9.8		0.3	2.0
4	KO vessel	Desiccant	40	1.2	27.1	87.9	9.8		0.3	2.0
5	Compressor	Grid	40	8	26.6	89.7	10.0		0.3	<0.01
6	CO_2 desorber	Emission	104–128	1	18.8		90.9			9.1
7	KO vessel	Condensate	40		0					
8	Desiccant regeneration	H_2S scavenger	78	1	4.1	76.1	8.5		0.3	15.1

presented is not intended as a direct comparison between Lewatit and PEI/SiO_2, nevertheless some observations can be made when comparing the two results. At the optimal operating conditions the heat demand for regeneration is a bit higher for the PEI/SiO_2, while the cyclic capacity of both sorbents is very similar.

It can be concluded that the shape of the isotherm can have a significant impact on the optimal working conditions, especially as both systems have significantly different optimal working temperatures. An accurate measurement of the isotherm is therefore essential. Especially at a very low partial pressure the isotherm is very steep and a small change in the isotherm can have a significant impact on the cycle. This shows the power of a combined experimental study with process design. From Figs. 10 and 11, it

Table 9
Key performance indicators of SAS and amine scrubbing.

KPI	Lewatit	PEI/SiO_2	Amine scrubbing
Q without heat integration (GJ/ton CO_2)	4.2	4.6	7.5 (3.9 in. L/R HX)
SRPEU	20%	22%	38%
Productivity (mol/m^3 s)	0.21	0.22	4.4

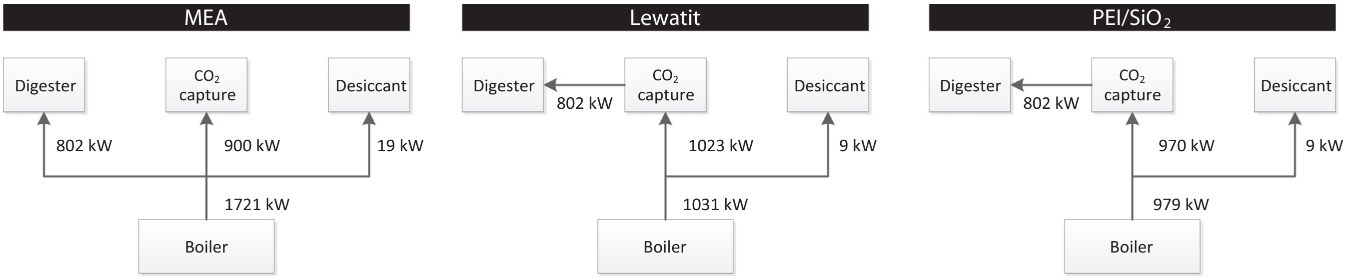

Fig. 12. Heat balance of the separate units.

can be seen that at operating conditions other than at the optimum, the regeneration heat can have a very high value.

The optimum process conditions from Aspen simulation were then used to calculate the fixed bed contactor size and productivity for SAS system. The results are given in Table 9.

3.3. System modeling of biogas upgrading with SAS

With the details of the SAS simulations, the systems model was run. Fig. 12 shows the energy balance of the systems analysis, a pinch analysis of which is shown in Appendix B. At the selected operating conditions, the contribution of the sensible heat and the heat for adsorption in the regeneration heat are of equal importance. The amount of water adsorbed is very low compared to the amount of CO_2 and consequently the contribution of water desorption in the regeneration heat is low. A special characteristic of the SAS is available at high temperature so it can be utilized by means of an intermediate heat transfer medium loop working with e.g. hot water, thermal oil or steam. This heat can be transported to the fermenter, covering a large part of its heat demand. By doing so the overall heat demand of the system is lowered significantly. Aqueous amine solvent technologies reject this heat at much lower temperatures, which makes that for a large part of this heat release only air or water cooling is an option and which makes the heat integration with the fermenter impossible.

The envisaged fixed bed adsorber, therefore needs to be equipped with heat exchange tubes, in which the heat is transferred to a heat transfer medium loop. During regeneration the same tubes can be used to supply the heat for regeneration. A valve system is required to switch between adsorption and regeneration. For fixed beds such designs are available, but tailoring towards the specific size and demands for the SAS system will be required.

The stream table (Table 8) shows the compositions of the most important streams in the flowsheet (Fig. 1). The digester is assumed to have a heat requirement of 15% of the lower heating value of the produced gas, as discussed in Section 2.3.1. For the current system that translates into 802 kW at 60 °C of heat demand, but that heat is fully supplied by the SAS system. Thus, in the SAS cases, the digester does not require direct heat input from the boiler (Fig. 12). Note that the geometry and size of the SAS are not currently specified, and these are subject to further optimization, but indicatively for a fluidized bed system a solids recirculation rate of approximately 9.5 kg s^{-1} would be required, whereas a fixed bed system with an estimated cycle time of 16 min. could require roughly 4600 kg of sorbent material. The desulphurisation does not require energy input, only periodic exchange of the material. The SAS system, as discussed above, has a heat requirement of 4.2–4.6 GJ/ton CO_2 (876–970 kW). For regeneration of the desiccant, 11% of the wet product gas (stream 4) is used and heated to 250 °C, consuming 9 kW of heat, which is negligible compared to the total energy consumption. The compression consumes an estimated 61 $kW_{electric}$, which can be expressed as 140 kW of heat (primary energy). The upgrading system thus consumes 1087–1186 kW of heat, which translates into a specific relative primary energy use (SRPEU) of 20% for Lewatit and 22% for PEI/SiO_2.

Most important for energy savings is the heat integration with the fermenter. The pinch analysis shows that this can be done because the heat is available at a higher level than in conventional amines systems. Optimizing the system further by reducing of the regeneration energy in the SAS system will not lead to overall energy savings, since an equivalent amount of energy would be required to heat the fermenter. Vice versa, there is a window to operate the SAS at a lower temperature, i.e. less efficient yet presumably more stable; as long as the rejected heat can be integrated with the fermenter (which is the case for an adsorber temperature > 60 °C), the SRPEU will not increase.

3.4. Technical evaluation

Table 9 presents the energy requirement without heat integration of the SAS system, the SRPEU, and volumetric productivity for both sorbents and for amine scrubbing. When the energy requirement of SAS (4.2–4.6 GJ/ton CO_2) is compared to that of the conventional amine scrubbing process (7.5 GJ/ton CO_2) it is clear that with regard to energy consumption, the SAS system is very promising. Liquid amine systems have a lean/rich heat exchanger (L/R HX) to decrease the reboiler duty, and such a solid–solid heat exchanger may also be applied for the SAS system to further reduce the energy consumption. The energy requirement for the SAS system without heat integration is already comparable with a conventional amine system with heat integration.

Given that heat integration with the fermenter was found to be of primary importance, the case presented in the unit operation assessments has been optimized further for heat integration. It is found that the heat integration effectively lowers the SRPEU to 20–22% depending on which sorbent is used. When these numbers are compared to amine scrubbing, the energy use and final sales gas flow can be expressed as specific relative primary energy use as well. For the amine scrubbing this is 38% SRPEU. Hence, the SAS system requires less primary energy than the amine scrubbing technology.

The productivity of SAS system (0.21–0.22 mol/m^3 s) are lower than amine scrubbing (4.4 mol/m^3 s). However, with respect to equipment size, the pre-selected fixed bed option is not optimal. It may be preferred from an ease of operation point of view, but to minimize equipment size an alternative configuration (e.g. trickle bed adsorber or multistage fluidized bed) is more attractive. This latter is not evaluated in further detail.

4. Conclusion

In this paper experimental work was combined with process and system studies to evaluate the potential of a SAS based CO_2

removal system for biogas upgrading. The experimental data were combined in a process model of a SAS system, and used to optimize the process cycle to a minimum energy consumption. Because of the temperature-independent heat of adsorption of PEI/SiO_2 and its unusual adsorption behavior at low temperatures, the studied sorbents had very different optimum cyclic designs. Also the shape of the isotherm was shown to have a significant impact on the optimal working conditions.

In the systems studies it was found that a SAS-based system offers the prospect of a significant energy demand reduction in biogas treatment, when compared to a reference amine scrubbing technology. With proper heat integration a reduction of Specific Relative Primary Energy Use (SRPEU) from 38% to 20–22%, can be achieved. The primary reason is that the heat rejected in the adsorber can be used for covering the heat demand of the fermenter, since SAS have higher optimal working temperatures than conventional amine systems. The optimum CO_2 adsorption and regeneration temperature depend upon the sorbent used. Operating the process below the optimum temperature level with marginal negative impact on the overall system energy demand is possible, as long as the heat integration with the fermenter can be sustained. The study shows the advantages of an integral experimental-process-systems study, and that SAS are a promising technology option for biogas upgrading. However, prior to industrial application of SAS technology for biogas upgrading, the low productivity issue due to the preselected fixed bed reactor type needs to be addressed.

Acknowledgements

The authors thank Dutch Ministry of Economic Affairs and cluster partners for financial support, and ISPT. Shell Global Solutions International B.V. is acknowledged for the TGA-DSC measurements of the heat of adsorption. Evert Wesker, Ries Janssen, Roberta Pacciani, Jacco Mooijer, Geert Versteeg and Ed Van Selow are acknowledged for discussions, and Gerard Elzinga and Özlem Pirgon-Galin for performing experimental work.

Appendix A. Amine simulation

The amine simulations have been done using ProTreat, a mass transfer rate-based simulator (version 5.5, GUI build 5.5.004), [23] and a typical amine flowsheet (Fig. A.1). Feed gas is compressed to 1.3 bar, regeneration is done at atmospheric pressure with overhead vapors being condensed at 40 °C. The lean/rich heat exchanger has an approach of 5 °C and a pressure drop of 0.3 bar. Monoethanolamine (MEA, 27%-w) is used as solvent, cooled to 50 °C and boosted to 1.5 bar before the absorber. Solvent flow is minimized to a maximum rich loading of 45%. The absorber and the regenerator are packed with 3 m structured packing (MellaPak 250 Y, with a diameter based on 70% flooding (sizes in Table A.1).

The regeneration duty ratio is started on 100 kW/(m^3/h solvent), and once the product gas is within specifications, the duty ratio and absorber height are decreased until spec is reached (reboiler temperature = 107 °C). Because of limitations on rich

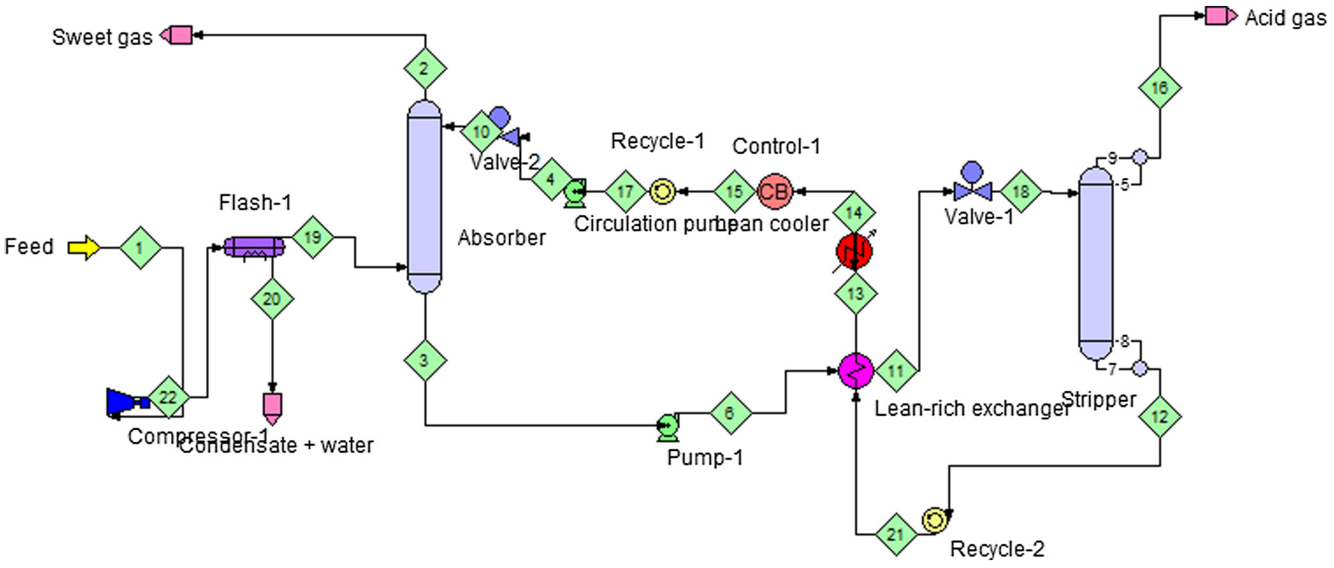

Fig. A.1. Screenshot from the ProTreat amine simulations.

Table A.1
Size and energy consumption of the amine scrubbing with MEA.

Size			Duty		
Absorber	0.51 × 3.0	m ID × m H packing	Reboiler duty	900	kW
Regenerator	0.56 × 3.0	m ID × m H packing	Condenser duty	370	kW
Volume	1.35	m^3	Solvent cooler duty	549	kW
			Solvent pump duty	1	kW
CO_2 removed	4.66	mol/s	Total electric power	599	kW
Productivity	3.45	mol/s/m^3	Total primary energy	11.6	GJ/ton acid gas

loading (loading < 0.45), the solvent flow had to be increased, decreasing the CO_2 concentration in product gas to 4.5% (instead of 10%).

Lean amine pump boosts the pressure to 1.5 bar, and the rich amine pump boosts the pressure sufficiently to overcome pressure drop in the lean/rich heat exchanger and static height of the columns. Columns have been sized using Frames internal design rules. Energy duties and sizes for the MEA design are noted in Table A.1.

The MDEA design was made using 35–40%-w MDEA only, and also activated with 1%-w piperazine. In these cases the absorber would become prohibitively high, and also require more regeneration duty.

Appendix B. Pinch analysis

Heat integration with a temperature approach of 10 °C was performed in a pinch analysis. The hot and cold composite curves for the Lewatit case (Fig. B.1), the PEI/SiO_2 case (Fig. B.2), and the amine scrubbing case (Fig. B.3) are shown below.

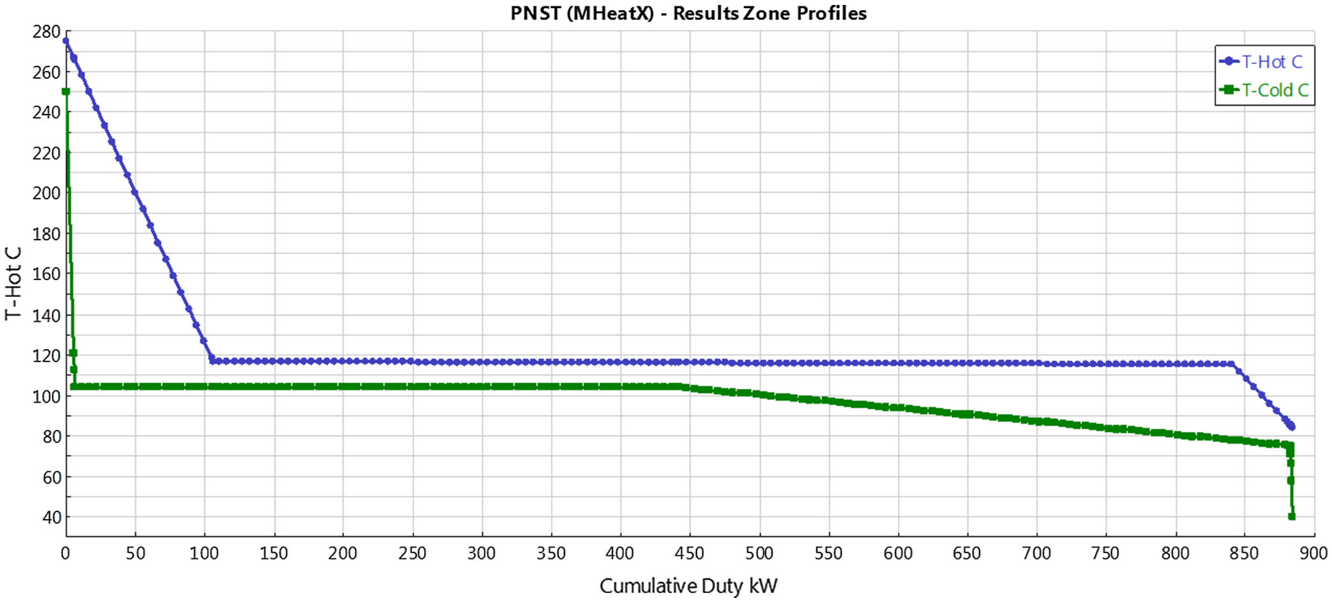

Fig. B.1. Hot and cold composite curves for Lewatit.

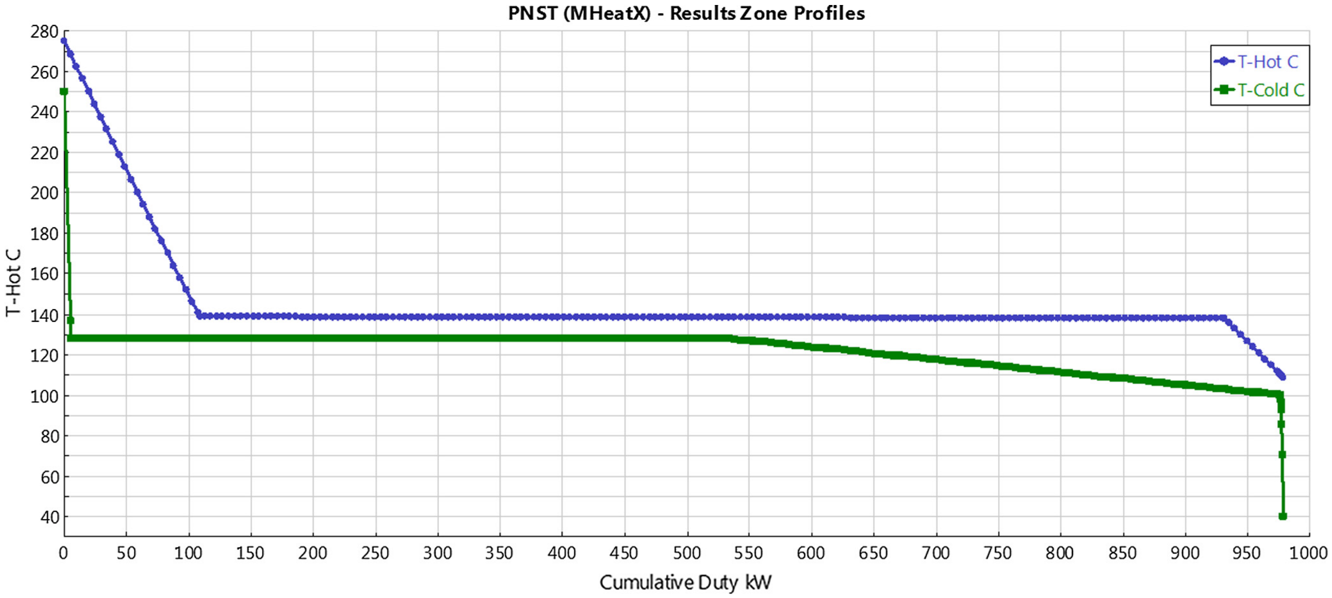

Fig. B.2. Hot and cold composite curves for PEI/SiO_2.

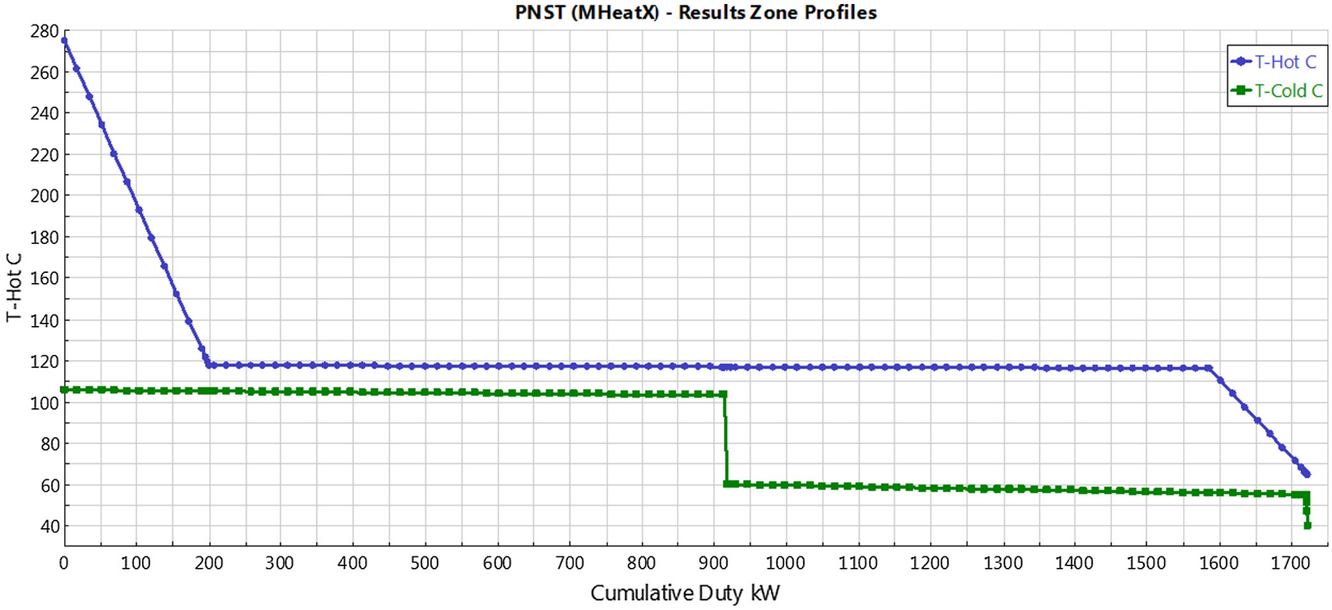

Fig. B.3. Hot and cold composite curves for amine scrubbing.

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