

GHGT-11

Post-Combustion CO₂ capture using supported amine sorbents: A process integration study

R. Veneman^{a*}, H. Kamphuis^b, D.W.F. Brilman^a

^aUniversity of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

^bDNV-KEMA, PO Box 9035, 6800 ET Arnhem, The Netherlands

Abstract

We have evaluated the feasibility of supported amine sorbents (SAS) for their application in post-combustion CO₂ capture. For this, the energy efficiency of a power plant equipped with a supported amine based capture facility is compared with the energy efficiency of a power plant equipped with a standard MEA-capture facility using the Spence[®] software tool developed by DNV-KEMA. Based on the simulations performed, application of a SAS-based capture facility at a natural gas combined-cycle (NGCC) plant is potentially 19% more energy efficient than a MEA-capture facility. For a pulverized-coal (PC) plant, the SAS-based plant could save up to 32% of the energy required in the MEA process.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and/or peer-review under responsibility of GHGT

Keywords: CO₂ capture, supported amine sorbents, NGCC, PC, energy efficiency

1. Introduction

Application of carbon capture and storage (CCS) at fossil fuel burning plants could significantly reduce the global emission of anthropogenic CO₂. However, using the current state-of-art technology, this would result in an increase in the cost of electricity by 35-85%, mainly due to high cost of CO₂ capture which are making up around 80% of the total cost of CCS [1]. This large increase in cost of electricity is considered unacceptable and the development of a more cost-effective capture technology is now the main objective of CO₂ capture research.

We aim to reduce the CO₂ capture costs by developing an adsorption based post combustion CO₂ capture process using supported amine sorbents (SAS), anticipated to have a lower energy requirement than the conventional amine scrubbing technology. A large part of the energy required in this absorption based process, is associated with heating of the aqueous amine solution from the absorption temperature to the desorption temperature and with the evaporation of solvent in the desorber column.

*Corresponding author. Tel.: +31 53 489 4418, Fax.: +31 53 489 4718
E-mail address: R.Veneman@utwente.nl

Replacing H₂O by a solid support greatly reduces the energy required for regeneration, due to the lower heat capacity of solid supports compared to water. In addition, the evaporation of water is prevented, reducing the process energy requirement even further.

Based on a process analysis study performed in this work, we concluded that an adsorption based capture process could potentially reduce the net energy requirement for CO₂ capture, from roughly 2.7 and 3.3 GJ.tCO₂⁻¹ for MEA scrubbing [2], to around 2 GJ.tCO₂⁻¹ using supported amine sorbents.

These supported amine sorbents consist of a high surface-area support with amine functional groups immobilized on or grafted to its surface [3]. Work has been done on optimization of these sorbent particles by tuning support characteristics, amine type and amine loading [4-8]. Porous carbon [9], zeolites [10], polymers such as poly(methyl methacrylate) and polystyrene [11], and silica's [12-14] are all considered as support candidates. Key strengths of these solid sorbents include: fast CO₂ uptake rates, high CO₂ capacities even at low CO₂ partial pressures, a low adsorption heat and relatively mild regeneration conditions.

In this work, we investigate the feasibility of supported amine sorbents for post combustion CO₂ capture by combining experimental work with a process simulation study. In the experimental section of this work, supported amine sorbents were prepared by physical impregnation of polymethylmethacrylate (PMMA) with tetraethylenepentamine (TEPA) and optimized with respect to amine loading and support pore size. The sorption characteristics of the developed sorbent material were determined for a wide range of temperatures and pressures.

We studied the technical feasibility of sorbent regeneration at high pressure as an option to further improve the energy efficiency of this novel CO₂ capture process. Compression of the captured CO₂, required for cost effective transportation and storage, adds around 20-25% to the total electrical energy requirement of the CO₂ capture facility [15]. Releasing CO₂ at 5 bar in the sorbent regeneration step would reduce the electrical energy required for compression.

Results obtained from the experimental work were subsequently used as a basis for process analysis study based on the Spence[®] software tool developed by DNV-KEMA. The KEMA-Spence[®] tool has been developed specially for the power plant sector and is nowadays successfully applied in many CO₂ capture studies, including various integration studies. Using the Spence[®] software tool, we have evaluated the energy efficiency of a power plant equipped with this novel capture system with that of a reference power plant equipped with an MEA-based capture facility.

2. Experimental

Supported amine sorbents were prepared by physical impregnation of polymethylmethacrylate[®] (Diaion[™] HP-2MG, Aldrich) with tetraethylenepentamine (TEPA, Aldrich). The sorbent material was optimized with respect to amine loading and support pore volume yielding a sorbent with a CO₂ capacity of 3.8 mol.kg⁻¹ sorbent [16]. A NETSZCH STA 449 F1 Jupiter thermal gravimetric analyzer (TGA) was used to assess the adsorption and desorption performance of the prepared sorbents.

Adsorption isobars of the developed sorbent material are presented in Figure 1. The sorbent sample was heated from 40°C up to 140°C at a heating rate of 0.1 K.min⁻¹ in 1 vol.%, 5 vol.%, 10 vol.% and 80 vol.% CO₂ atmosphere (balance N₂) at a total flow rate of 100 ml.min⁻¹. As the specific configuration of the TGA equipment limited the CO₂ concentration to a maximum of 80 vol.% of CO₂ at 1 atm, therefore desorption experiments in pure CO₂ were not performed. Sorbent operating capacities were calculated for two different cases; CO₂ capture at a natural gas combined cycle (NGCC) plant and CO₂ capture at a pulverized coal (PC) plant.

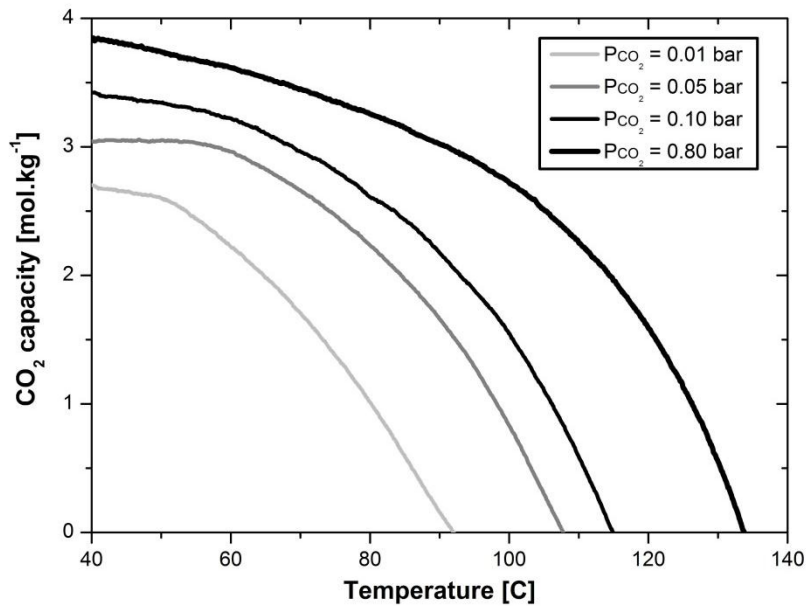


Figure 1: Adsorption isobars in 1vol.%, 5vol.%, 10vol.% and 80 vol.% CO₂ (P_{total} = 1 bar).

Flue gas from a NGCC plant typically contains around 4-7 vol% of CO₂ whereas flue gas from PC plant contains around 10-15vol% of CO₂. For adsorption at 60°C, the sorbent working capacity was calculated as the difference between the CO₂ capacity under adsorption conditions and the CO₂ capacity at elevated temperatures, in 80vol% CO₂, given by the adsorption isobars presented in Figure 1.

Capturing CO₂ from flue gas containing 10 vol.% for adsorption of CO₂ at 60°C and desorption in 80 vol.% CO₂ at 130°C working capacities of around 3.1 mol.kg⁻¹ sorbent can be achieved using the developed sorbent. For capture from flue gas containing 5 vol.% of CO₂, working capacities up to 2.6 mol.kg⁻¹ sorbent can be achieved under same adsorption and desorption conditions. As releasing CO₂ at elevated pressure in the sorbent regeneration step would reduce the electrical energy required for compression of CO₂, high pressure desorption experiments were performed in a fixed bed set-up to study the technical feasibility of this regeneration concept. CO₂ was captured from simulated flue gas containing 6.7 vol.% of CO₂ (balance N₂, 1 bar) at 40°C. During sorbent regeneration, the CO₂ pressure inside the reactor was controlled using a back pressure regulator. Concluding from Figure 2, the sorbent can successfully be regenerated at elevated CO₂ partial pressures (up to 10 bar). Part of the CO₂ adsorbed by the developed sorbent, around 0.6 mol.kg⁻¹ sorbent, can already successfully be released in 5 bar CO₂ at 140°C. The rest of the CO₂ captured is released when the CO₂ pressure is subsequently lowered to 1 bar.

Based on these experimental results, a two-step regeneration scheme seems attractive; e.g. a first regeneration step at 5 bar CO₂, followed by near complete sorbent regeneration at 1 bar CO₂. In this way, 10% of the CO₂ compression energy can be saved. To regenerate the sorbent at higher pressures, slightly higher regeneration temperatures are required for achieving the same operating capacities introducing a trade-off between the electrical energy input and the thermal energy input of adsorption based capture system. It should be noted that the sorbent's thermal and chemical stability needs to be improved to allow for sorbent regeneration under these conditions. This is the focus of current research at the University of Twente.

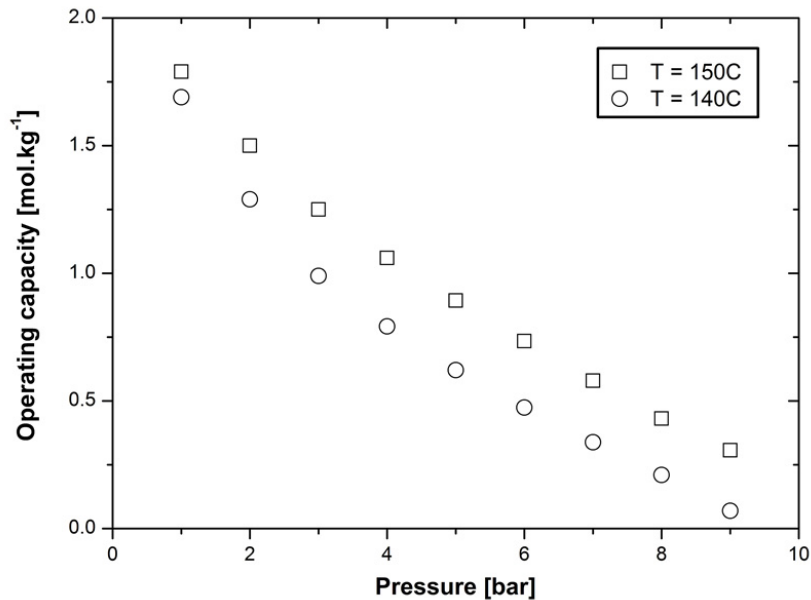


Figure 2: Sorbent operating capacity as a function of the regeneration pressure at regeneration temperatures of 140°C and 150°C

3. Methodology

Within DNV-KEMA an in-house software tool is available, which is developed and utilized for the conceptual design and integration of CO₂ capture plants with existing power plants; the Spence[®] model. The KEMA-Spence[®] model has been successfully applied in many CO₂ capture studies, including integration studies.

In this work, the Spence[®] software tool is used for four integration cases. In this feasibility study, the MEA scrubbing technology was treated as benchmark technology. A standard NGCC plant and a PC plant both equipped with an optimized MEA-based capture facility were simulated. The simulation results were compared with those for simulations of the NGCC plant equipped with a supported amine based capture facility and the PC plant equipped with a supported amine based capture facility. In this comparison, attention is focused on the amount of electrical energy consumed by the capture facility per unit mass of CO₂ captured of a power plant equipped with this novel capture systems relative to a reference power plant equipped with an MEA-based capture facility. Additionally, we evaluated the upside potential for the solid sorbent capture process and also the impact of the most important process parameters like: sorbent operating capacity, regeneration temperature and regeneration pressure.

The NGCC plant has a net power output of 446 MW. The PC plant produces 1068 MW. The thermal energy required for solvent/sorbent regeneration is extracted from the power plant's low pressure steam cycle at 4.6 bar and 3.5 bar for the NGCC plant and the PC plant respectively.

4. System design

General information regarding the CO₂ capture facility are summarized in Table 1. Although the system boundary of interest here does not include CO₂ transport and storage systems, CO₂ compression is assumed to occur within the facility boundaries. The model of the CO₂ compression is made of 8-stages

compression. 8 compression stages was found optimal for this application considering the trade-off between power consumption and investment costs. The first five stages of compression are equipped with condensate removal devices to extract water that condenses during cooling. After the first five stages a Tri-Ethylen-Glycol (TEG) Dewatering process reduces the water content below the limit set by pipeline restrictions (50 ppmw). The compression is then completed with three additional intercooled compressors. The pressure ratio is assumed to be the same for each compression stage.

Table 1: Capture plant general data

Parameters	NGCC	PC
Flue gas CO ₂ content (vol.%)	4.4	13.7
CO ₂ captured (kg/s)	38.0	202.3
Capture efficiency (%)	90	90
CO ₂ purity (%)	95	95
Pressure CO ₂ product stream (bar)	110	110

4.1 MEA-capture facility:

The MEA-based capture facility was modelled as a standard regenerative absorption-desorption system using a MEA absorption liquid with a net thermal energy input of 3.0 GJ.tCO₂⁻¹. Values for the heat requirement for the leading absorption technologies are between 2.7 and 3.3 GJ. GJ.tCO₂⁻¹, depending on the solvent process [2]. The absorber and desorber column were operated at 110 kPa and 40°C and 170 kPa and 118°C respectively. The MEA system pressure drop is 81.5 mbar for the PC system and 40 mbar for the NGCC system. In the electrical energy requirement of the capture system includes the energy required for (1) the flue gas blower, (2) the pumps to circulate the absorption liquid from the absorber to the desorber column and v.v. and (3) the CO₂ product gas compressor.

4.2 SAS-capture facility:

The supported amine capture facility was modeled as a regenerative adsorption-desorption system with the sorbent material circulating between the adsorber and desorber column. Both columns are operated at atmospheric pressure with the adsorber column operated at 60°C and the desorber column at 130°C. The system pressure drop in the absorber and desorber column is calculated based on a dual fluid bed design including the static pressure drop of the bed and the pressure drop over the gas distributor. The system pressure drop was calculated to be 170mbar. The thermal energy input of the supported amine capture facility was calculated based on the methodology developed by Li et. al. [17]. The thermal energy input equals the sum of the desorption heat, equal to 1.5 GJ.tonne⁻¹ CO₂ [18], and the sensible heat required to heat the sorbent material from the adsorption temperature up to the desorption temperature.

The sensible heat energy requirement is a function of the heat capacity of the sorbent material (1.5 KJ.kg⁻¹.K⁻¹), the temperature difference between the adsorption column and the desorber column (70K) and the working capacity of the sorbent material.

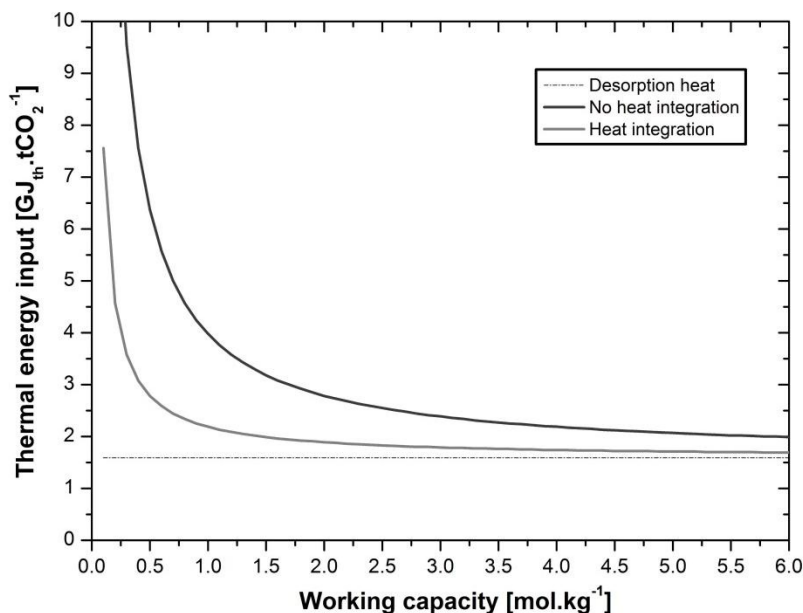


Figure 3: Thermal energy input of the SAS-capture facility

In Figure 3, this net thermal energy requirement of the process is plotted as a function of the sorbent operating capacity. From these energy calculation it was concluded that application of this process could potentially reduce the thermal energy requirement for CO₂ capture, from 3 GJ.tCO₂⁻¹, for MEA scrubbing, to around 1.8 GJ.tCO₂⁻¹ at sorbent operating capacities between 2.6-3.1 mol.kg⁻¹. These values are 40% lower than the values reported for MEA-based systems with advanced stripper configurations and 30% lower than the lowest values reported for the KS-1 solvents by MHI [15]. In these calculations it was assumed that 75% of the sensible heat required for heating the sorbent material can be recovered indirect or direct in a solid-solid heat exchanger. For comparison, the liquid-liquid heat exchanger in the MEA process is capable of reusing around 90% of the sensible heat. Moreover, in these calculations the possible co-adsorption of water in the adsorber column, is not taken into account.

Concluding from Figure 3, at working capacities higher than 2 mol.kg⁻¹ the reaction heat will dominate the thermal energy demand of the SAS-based capture facility. Increasing the operating capacity further will not result in a substantial further decrease the thermal energy requirement of the SAS-capture system. In the electrical energy requirement calculated for the capture system, the power consumption of the flue gas blower, the energy required to circulate the sorbent from the absorber to the desorber column and the energy required for compression of the CO₂ product stream are included.

5. Process analysis results

Based on the energy calculation performed in section 4.2 application of the adsorption based capture process can potentially reduce the thermal energy requirement for CO₂ capture from 3 GJ.tCO₂⁻¹ to around 1.7 GJ.tCO₂⁻¹. Using the Spence[®] software tool, a standard NGCC plant and a PC plant both equipped with an optimized MEA-based capture facility were simulated and compared on energy basis with simulation of the NGCC plant equipped with a supported amine based capture facility and the PC

plant equipped with a supported amine based capture facility. The main results of the simulations are summarized in Table 2.

Table 2: Spence[®] simulation results

Plant data	NGCC			PC		
	Ref.	MEA	SAS	Ref.	MEA	SAS
Heat input (MWth)	756.7	756.7	756.7	2307.3	2307.3	2307.3
Gross power (MWe)	452.4	408.2	431.1	1116.7	935.9	1031.8
Net power (MWe)	445.5	384.2	395.8	1068.6	804.0	889.0
Own consumption (MWe)	6.0	5.1	5.6	45.9	46.0	45.9
Transformer losses (MWe)	0.9	0.8	0.8	2.1	1.6	1.8
Capture plant electricity demand (MWe)	-	6.0	15.3	-	19.9	22.2
CO ₂ Compression (MWe)	-	12.1	13.6	-	64.5	72.9
Emission rate (tCO ₂ .MWh ⁻¹)	0.37	0.04	0.04	0.84	0.11	0.11
Net plant Efficiency (%)	58.9	50.8	52.3	46.3	34.8	38.5
Required extra input (% of MWth)	-	16.0	12.7	-	33.0	20.2

Since a PC plant emits 2.7 times more CO₂ per MWh than a NGCC plant, due the lower heating value of coal compared to gas, application of CO₂ capture at a PC plant has a higher impact on the plant power output. To compensate for the lower power output, a NGCC-MEA plant requires 16% more input compared 33% for a PC-MEA plant. The installation of a capture facility at a power plant results in a decrease in power output as steam is extracted from the power plant for solvent and sorbent regeneration. However, due to the lower thermal energy requirement of the sorbent based process, the loss in gross power is less than half of the power lost when a solvent based process is installed. A NGCC-SAS plant requires 12.7% more input and a PC-SAS plant 20.2% more compared 16% and 33% for the MEA-based equivalent.

In Figure 4, the electricity demand of the capture facility is plotted for each case study performed. The column labeled as ‘NGCC-minimum’ and ‘PC-minimum’ represent the thermodynamic minimum work required for CO₂ separation and compression to 110 bar. The ‘Desorption’ energy, in Figure 4, is related to the decrease in the electrical energy output of the power plant caused by the extraction of steam for sorbent/solvent regeneration. The ‘Electrical’ energy includes (1) energy for sorbent/solvent circulation and (2) the power demand of the flue gas blower. The ‘Compression’ energy is related to the power consumption of the CO₂ compressor. Concluding from Figure 4, installation of a SAS-based capture facility at a NGCC plant is 19% more efficient on an energy basis than a MEA-based capture facility. For a PC plant a sorbent based plant is 33% more efficient.

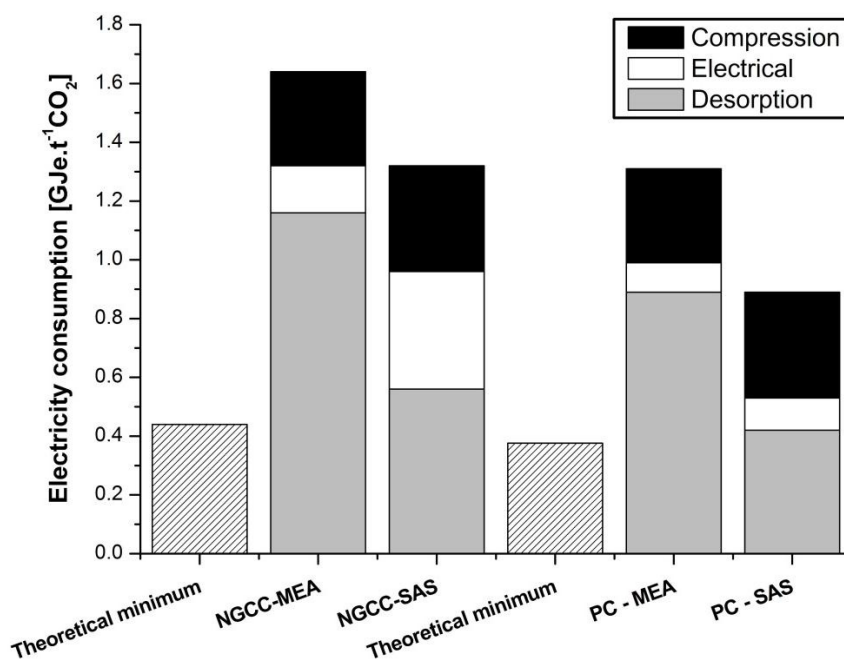


Figure 4: Break down of the capture facility electricity consumption.

The two biggest electricity consumers within the power plant (including the capture facility) are the CO₂ compressor and the flue gas blower. The flue gas blower is dominating the capture plant's electricity demand, especially for the sorbent based capture at a NGCC plant. This is mainly due to the higher pressure drop for sorbent based capture and the higher flue gas flows at a NGCC plant. Designing a system with a low pressure drop could further reduce the energy requirement. Additionally, high pressure sorbent regeneration can save 10 vol% of the CO₂ compression energy. This will further reduce the overall capture energy with around 5%.

6. Conclusions

We have investigated the feasibility of supported amine sorbents for post combustion CO₂ capture by combining experimental work with a process analysis study. Supported amine sorbents, prepared by physical impregnation of PMMA with TEPA, were tested experimentally for application in post-combustion CO₂ capture, especially with respect to cyclic capacity and the feasibility of high pressure sorbent regeneration. Using the developed sorbent we can potentially reduce the thermal energy requirement for CO₂ capture from 3 GJ.tCO₂⁻¹ to around 1.7 GJ.tCO₂⁻¹. Using the Spence[®] software tool, developed by DNV-KEMA, we have evaluated the energy efficiency of a power plant equipped with this novel capture systems to that of a reference power plant equipped with a MEA-based capture facility. Installation of a SAS-based capture facility at a NGCC plant is 19% more efficient of an energy basis than a MEA-based capture facility. For a PC plant a sorbent based capture plant is 33% more efficient.

Acknowledgement

This research is part of the CATO2 programme, the Dutch national research programme on CO₂ Capture and Storage. CATO2 is financially supported by the Dutch Ministry of Economic Affairs (EZ) and the consortium partners (www.co2-cato.nl). We kindly acknowledge Benoît Thomas for his contribution and Dr. Bert Heesink (DNV-KEMA) for initiating the project.

References

- [1] Brunetti A, Scura F, Barbieri G, Drioli E, Membrane technologies for CO₂ separation, *Journal of Membrane Science*, 359 (2010) 115-125.
- [2] Mathieu P, The IPCC special report on carbon dioxide capture and storage, *ECOS 2006: Proceedings of the 19th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, Vols 1-3*, (2006) 1611-1617.
- [3] Ebner AD, Gray ML, Chisholm NG, Black QT, Mumford DD, Nicholson MA, Ritter JA, Suitability of a solid amine sorbent for CO₂ capture by pressure swing adsorption, *Industrial and Engineering Chemistry Research*, 50 (2011) 5634-5641.
- [4] Chen C, Yang ST, Ahn WS, Ryoo R, Amine-impregnated silica monolith with a hierarchical pore structure: Enhancement of CO₂ capture capacity, *Chem Commun*, (2009) 3627-3629.
- [5] Heydari-Gorji A, Yang Y, Sayari A, Effect of the pore length on CO₂ adsorption over amine-modified mesoporous silicas, *Energy and Fuels*, 25 (2011) 4206-4210.
- [6] Kim S, Ida J, Gulians VV, Lin JYS, Tailoring pore properties of MCM-48 silica for selective adsorption of CO₂, *J Phys Chem B*, 109 (2005) 6287-6293.
- [7] Belmabkhout Y, Sayari A, Effect of pore expansion and amine functionalization of mesoporous silica on CO₂ adsorption over a wide range of conditions, *Adsorption*, 15 (2009) 318-328.
- [8] Ko YG, Shin SS, Choi US, Primary, secondary, and tertiary amines for CO₂ capture: Designing for mesoporous CO₂ adsorbents, *Journal of Colloid and Interface Science*, 361 (2011) 594-602.
- [9] Houshmand A, Daud WMAW, Lee MG, Shafeyyan MS, Carbon Dioxide Capture with Amine-Grafted Activated Carbon, *Water, Air and Soil Pollution*, (2011) 1-9.
- [10] Su FS, Lu CY, Kuo SC, Zeng WT, Adsorption of CO₂ on Amine-Functionalized Y-Type Zeolites, *Energy & Fuels*, 24 (2010) 1441-1448.
- [11] Gray ML, Hoffman JS, Hreha DC, Fauth DJ, Hedges SW, Champagne KJ, Pennline HW, Parametric Study of Solid Amine Sorbents for the Capture of Carbon Dioxide, *Energy & Fuels*, 23 (2009) 4840-4844.
- [12] Xu X, Andresen JM, Song C, Miller BG, Scaroni AW, Preparation of novel CO₂ "molecular basket" of polymer modified MCM-41, in, 2002, pp. 67-68.
- [13] Xu X, Song C, Miller BG, Scaroni AW, Influence of moisture on CO₂ separation from gas mixture by a nanoporous adsorbent based on polyethylenimine-modified molecular sieve MCM-41, *Industrial and Engineering Chemistry Research*, 44 (2005) 8113-8119.
- [14] Bhagiyalakshmi M, Yun LJ, Anuradha R, Jang HT, Synthesis of chloropropylamine grafted mesoporous MCM-41, MCM-48 and SBA-15 from rice husk ash: their application to CO₂ chemisorption, *J Porous Mat*, 17 (2010) 475-484.
- [15] Rochelle G, Chen E, Freeman S, Van Wagener D, Xu Q, Voice A, Aqueous piperazine as the new standard for CO₂ capture technology, *Chemical Engineering Journal*, (2011).
- [16] Veneman R, Li ZS, Hogendoorn JA, Kersten SRA, Brilman DWF, Continuous CO₂ capture in a circulating fluidized bed using supported amine sorbents, *Chemical Engineering Journal*, (2012).
- [17] Li ZS, Cai NS, Croiset E, Process analysis of CO₂ capture from flue gas using carbonation/calcination cycles, *Aiche J*, 54 (2008) 1912-1925.
- [18] Fauth DJ, Gray ML, Pennline HW, Krutka HM, Sjostrom S, Ault AM, Investigation of porous silica supported mixed-amine sorbents for post-combustion CO₂ capture, *Energy and Fuels*, 26 (2012) 2483-2496.