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## Post-Combustion CO<sub>2</sub> capture using supported amine sorbents: A process integration study

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### Abstract

We have evaluated the feasibility of supported amine sorbents (SAS) for their application in post-combustion CO<sub>2</sub> 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<sup>®</sup> 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.

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### 1. Introduction

Application of carbon capture and storage (CCS) at fossil fuel burning plants could significantly reduce the global emission of anthropogenic CO<sub>2</sub>. 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 CO<sub>2</sub> 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 CO<sub>2</sub> capture research.

We aim to reduce the CO<sub>2</sub> capture costs by developing an adsorption based post combustion CO<sub>2</sub> 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.

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Replacing H<sub>2</sub>O 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 CO<sub>2</sub> capture, from roughly 2.7 and 3.3 GJ.tCO<sub>2</sub><sup>-1</sup> for MEA scrubbing [2], to around 2 GJ.tCO<sub>2</sub><sup>-1</sup> 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 CO<sub>2</sub> uptake rates, high CO<sub>2</sub> capacities even at low CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> capture process. Compression of the captured CO<sub>2</sub>, required for cost effective transportation and storage, adds around 20-25% to the total electrical energy requirement of the CO<sub>2</sub> capture facility [15]. Releasing CO<sub>2</sub> 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<sup>®</sup> software tool developed by DNV-KEMA. The KEMA-Spence<sup>®</sup> tool has been developed specially for the power plant sector and is nowadays successfully applied in many CO<sub>2</sub> capture studies, including various integration studies. Using the Spence<sup>®</sup> 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<sup>®</sup> (Diaion<sup>™</sup> 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 CO<sub>2</sub> capacity of 3.8 mol.kg<sup>-1</sup> 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<sup>-1</sup> in 1 vol.%, 5 vol.%, 10 vol.% and 80 vol.% CO<sub>2</sub> atmosphere (balance N<sub>2</sub>) at a total flow rate of 100 ml.min<sup>-1</sup>. As the specific configuration of the TGA equipment limited the CO<sub>2</sub> concentration to a maximum of 80 vol.% of CO<sub>2</sub> at 1 atm, therefore desorption experiments in pure CO<sub>2</sub> were atmosphere were not performed. Sorbent operating capacities were calculated for two different cases; CO<sub>2</sub> capture at a natural gas combined cycle (NGCC) plant and CO<sub>2</sub> capture at a pulverized coal (PC) plant.

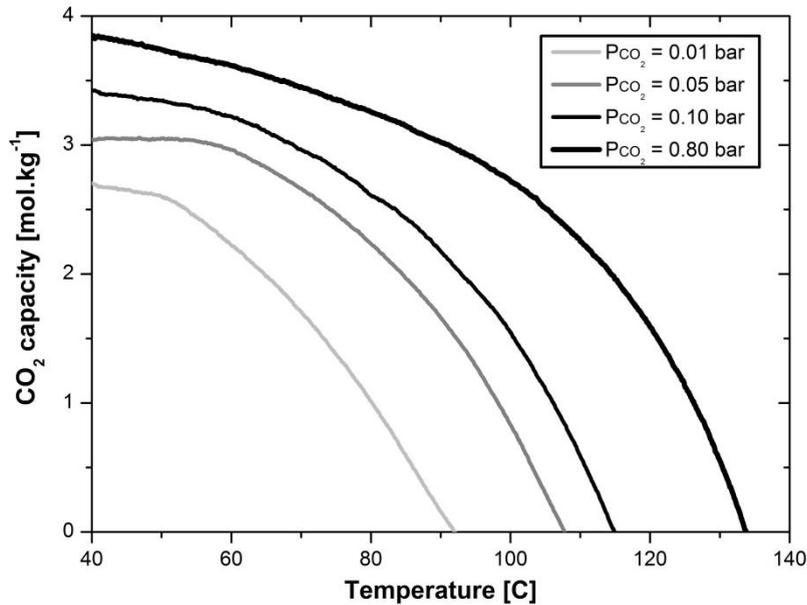


Figure 1: Adsorption isobars in 1vol.%, 5vol.% and 80 vol.% CO<sub>2</sub> (P<sub>total</sub> = 1 bar).

Flue gas from a NGCC plant typically contains around 4-7 vol% of CO<sub>2</sub> whereas flue gas from PC plant contains around 10-15vol% of CO<sub>2</sub>. For adsorption at 60°C, the sorbent working capacity was calculated as the difference between the CO<sub>2</sub> capacity under adsorption conditions and the CO<sub>2</sub> capacity at elevated temperatures, in 80vol% CO<sub>2</sub>, given by the adsorption isobars presented in Figure 1.

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

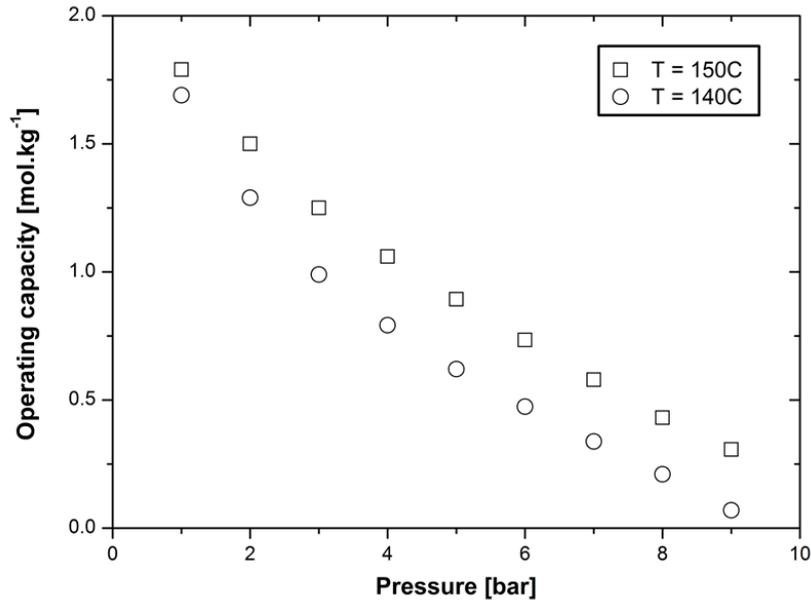


Figure 2: Sorbent operating capacity as a function of the regeneration pressure at regeneration temperatures of 140°C and 150°C

### 3. Methodology

Within DNV-KEMA an in-house software tool is available, which is developed and utilized for the conceptual design and integration of CO<sub>2</sub> capture plants with existing power plants; the Spence<sup>®</sup> model. The KEMA-Spence<sup>®</sup> model has been successfully applied in many CO<sub>2</sub> capture studies, including integration studies.

In this work, the Spence<sup>®</sup> 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 CO<sub>2</sub> 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 CO<sub>2</sub> capture facility are summarized in Table 1. Although the system boundary of interest here does not include CO<sub>2</sub> transport and storage systems, CO<sub>2</sub> compression is assumed to occur within the facility boundaries. The model of the CO<sub>2</sub> 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 <sub>2</sub> content (vol.%)	4.4	13.7
CO <sub>2</sub> captured (kg/s)	38.0	202.3
Capture efficiency (%)	90	90
CO <sub>2</sub> purity (%)	95	95
Pressure CO <sub>2</sub> 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.tCO<sub>2</sub><sup>-1</sup>. Values for the heat requirement for the leading absorption technologies are between 2.7 and 3.3 GJ. GJ.tCO<sub>2</sub><sup>-1</sup>, 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 CO<sub>2</sub> 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<sup>-1</sup> CO<sub>2</sub> [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<sup>-1</sup>.K<sup>-1</sup>), the temperature difference between the adsorption column and the desorber column (70K) and the working capacity of the sorbent material.

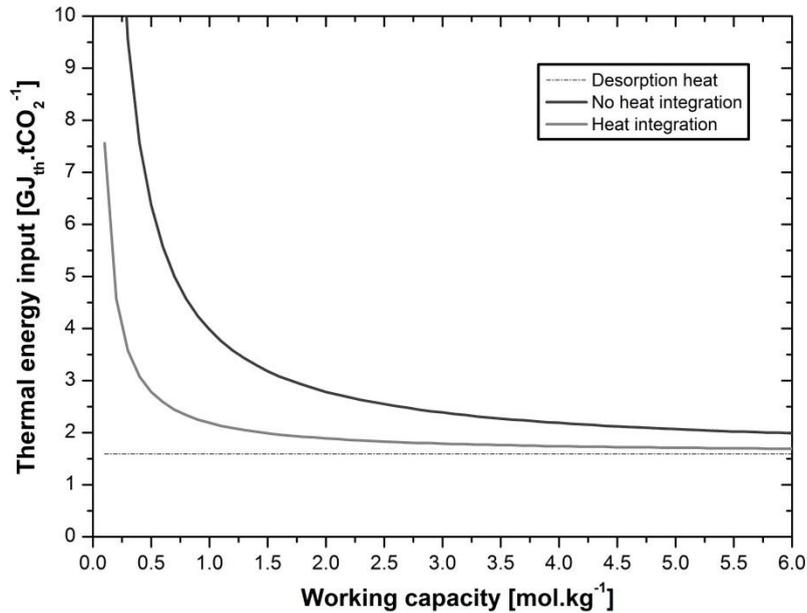


Figure 3: Thermal energy input of the SAS-capture facility

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 CO<sub>2</sub> capture, from 3 GJ.tCO<sub>2</sub><sup>-1</sup>, for MEA scrubbing, to around 1.8 GJ.tCO<sub>2</sub><sup>-1</sup> at sorbent operating capacities between 2.6-3.1 mol.kg<sup>-1</sup>. 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<sup>-1</sup> 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 CO<sub>2</sub> 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 CO<sub>2</sub> capture from 3 GJ.tCO<sub>2</sub><sup>-1</sup> to around 1.7 GJ.tCO<sub>2</sub><sup>-1</sup>. Using the Spence<sup>®</sup> 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<sup>®</sup> 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 <sub>2</sub> Compression (MWe)	-	12.1	13.6	-	64.5	72.9
Emission rate (tCO <sub>2</sub> .MWh <sup>-1</sup> )	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 CO<sub>2</sub> per MWh than a NGCC plant, due the lower heating value of coal compared to gas, application of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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.

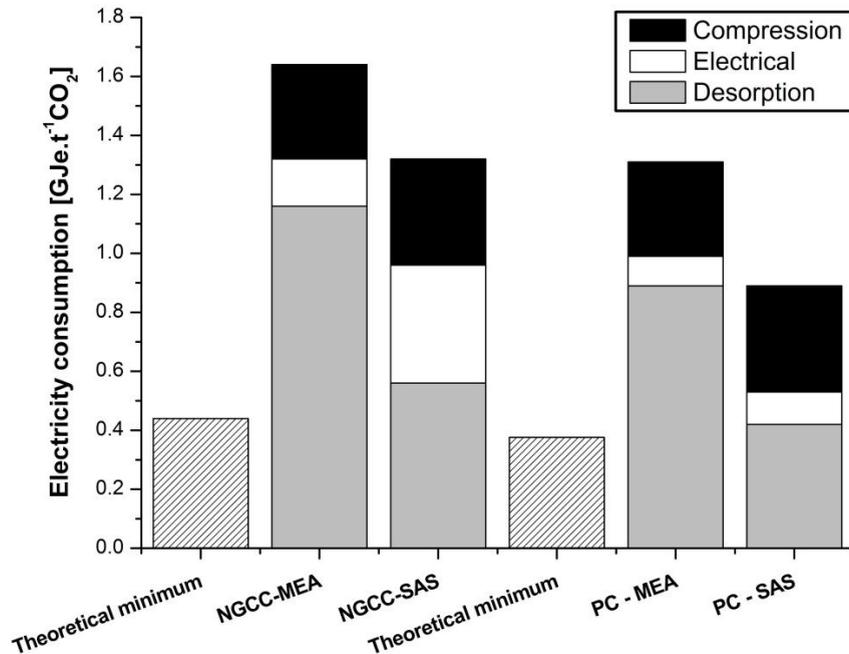


Figure 4: Break down of the capture facility electricity consumption.

The two biggest electricity consumers within the power plant (including the capture facility) are the CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> capture from 3 GJ.tCO<sub>2</sub><sup>-1</sup> to around 1.7 GJ.tCO<sub>2</sub><sup>-1</sup>. Using the Spence<sup>®</sup> 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.

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