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Techno-Economic Evaluation Methodology and Preliminary Comparison of an Amine-Based and Advanced Solid Sorbent-Based CO₂ Capture Process for NGCC Power Plants

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Abstract

The post combustion capture process using the traditional amine based solvent absorption process is a very mature technology that suffers from a high energy penalty being taken on the power plant and requires significant capital investment that causes us a high increase in the cost of electricity. An advanced solid-based adsorption is discussed in this work as well as a techno-economic evaluation methodology in order to compare the advantages of this novel process to the conventional process. Some indications of the expected technical and economic benefits of the process are also discussed.

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1. Introduction

Solvent based CO_2 Post-combustion capture (PCC) technology is the most widely adopted and established technology to deal with anthropogenic CO_2 emissions[1]. This is due to the process's high efficiency, high selectivity, scale-up feasibility, significant industrial experience in such processes for similar applications and its retrofitability to existing power plants with no change to the upstream power plant. Examples of this technology in industry include Fluor's Econamine process[2], Siemen's POSTCAP process[3] and Mitsubishi's KM-CDR process[4]. The major challenge for the conventional post-combustion capture process is the significant energy required to regenerate the solvent and the effect that implementing such a technology has on reducing the efficiency of the power plant and the high cost of electricity associated with the process. The amine based processes also pose an environmental concern

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due to the possibility of continuous amine emissions into atmosphere [5]. These barriers prevent large scale deployment of the capture process from large scale deployment and resulting in further research into alternative technologies to overcome these barriers.

Therefore, there is a need for the development of novel systems to capture the CO_2 . Solid-based capture processes are considered advantageous in comparison to the conventional solvent based process because they exhibit high CO_2 loadings (10-20 wt% CO_2), they have low heat capacities (1-1.5 kJ/kg-K), they are capable of generating high partial pressures of carbon dioxide without vaporizing significant quantities of water in the solvent and they often avoid the toxicity and volatility issues associated with the solvent system[6]. One such sorbent is the family of molecular basket sorbents (MBS) developed by Dr. Chushan Song's group at Pennsylvania State University (PSU) [7]. These supported amines, which consist of impregnated-and-grafted materials, have all the advantages of amine sorption (high CO_2 loading, high selectivity and rapid kinetics) without the high regeneration energy due to the absence of the heat associated with the vaporization of the water and sensible heat in the solvent case[7–9].

PSU's MBS sorbent consists of polyethyleneimine (PEI) on a high surface area support and is capable of high CO_2 loadings of approximately 14 wt % CO_2 and high CO_2/N_2 selectivity. The mechanism by which the absorption occurs is as follows:

Primary: $CO_2 + 2RNH_2 \leftrightarrow NH_4^+ + R_2NCOO^-$ Secondary: $CO_2 + 2R_2NH \leftrightarrow R_2NH_2^+ + R_2NCOO^-$ Tertiary: $CO_2 + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^-$

Besides optimization of the sorbent itself in terms of production cost, chemical/thermal stability, loading and attrition resistance, the challenges associated with the deployment of this technology include process/equipment development to ensure effective heat transfer from/to the sorbent absorption/regeneration systems, the fluidization of large quantities of the sorbent and the development of reactors that allow for effective gas-solid mass transfer and reasonable gas-side pressure drop[6]. Heat exchange requirements in both the absorption/desorption steps is well above what is achievable in fixed bed systems and hence fluidized bed becomes essential. RTI International, with financial support from the US DOE and Masdar Clean Energy, is working with PSU to develop this technology to be deployed in conjunction with coal-based power plants.

It is of significant interest to Masdar Clean Energy and the vision of the UAE to extend this technology to be applied to natural gas combined cycle (NGCC) power plants since natural gas is the fuel source used in power generation in the UAE. As one of the project partners, Masdar Institute's aim is to perform a techno-economic evaluation on the viability of both the advanced solid sorbent technology and aminebased solvent processes on flue gas emitted from natural gas combined cycle power plants. The concentration of CO_2 in NGCC flue gas is lower than in coal-fired power plant flue gas but the flue gas flow rate for a given CO_2 capture rate is higher. The techno-economic evaluation entails the following:

- 1. CO₂ post-combustion capture conventional process simulation, design and economic evaluation, which will be used for comparison purposes as a reference case;
- 2. Solid sorbent-based capture process simulation and design, adapting an Aspen simulation flow sheet developed by RTI for a coal-based power plant case;
- 3. Solid sorbent-based capture process preliminary economic evaluation and comparison with the conventional capture process. The economic evaluation and comparison will consider the capital costs, operational costs, overall capture cost and the increase in the cost of electricity. In addition, the techno-economic behaviour of the solid sorbent-based process for the NGCC case will be compared with the coal-fired power plant case.

To date, much of the work has been focused on fully optimizing, costing and ensuring that our simulation and economic analysis of a conventional CO_2 capture process (based on monoethanolamine solvent) applied to NGCC flue gas is accurate and matches a case study performed and reported by the US DOE (Case 13 of the report)[10]. Also, work is currently on going with the simulation and economic analysis of the solid case for NGCC application. Aspen Plus is being used for the simulation,. The process overview descriptions for the solid case as well as the conventional process will be provided in subsequent sections. Additionally, costing methodology and assumptions will be covered as to lay the groundwork for the economic assumptions being used in this work and for future work. Finally, the expected outcomes will be mentioned based on the initial findings of simulation work and from work done on simulating the solid sorbent-based process with coal-based power plants. The economic results may be further refined by future work where laboratory, CO_2 capture studies will be carried out using a representative bench-scale process system to approximate both coal plant and NGCC conditions.

2. Solid Sorbent Technology Overview

RTI International, PSU, and other project partners are working to advance the feasibility of using solid molecular basket sorbent technology for post-combustion flue gas applications. To date, PSU has demonstrated that their initial MBS materials are capable of achieving high CO₂ loadings, high CO₂/N₂ selectivity, exhibit a reasonable heat of absorption (66 kJ/mol CO₂), and can be prepared from inexpensive high surface area support materials. The MBS absorbent has previously been prepared by loading sterically branched PEI, which consists of branched chains with numerous amine groups (primary, secondary and tertiary amines) onto a high-surface-area nano-pore material, such as MCM-41 and SBA-15, which have parallel-arranged pore channels. The sorbent absorbs CO₂ via carbamate and bicarbonate chemical reaction pathways. CO₂ absorption is favoured between 50-90 °C. At temperatures above 110 °C (230 °F), the reverse reactions predominate and the sorbent releases CO₂.

Although PSU's MBS materials exhibited many desirable CO_2 capture performance characteristics, the materials have not been optimized for a specific solids-based CO_2 capture process design. In addition, the MBS materials have some remaining development challenges which include: improving the thermal and chemical stability and reducing the production costs of the materials. RTI and PSU are focused on addressing these challenges through novel sorbent production pathways (e.g. cross-linking approaches, enhanced support-PEI interaction) and selection of lower cost starting materials. In parallel to these sorbent development efforts, RTI is developing and evaluating the most promising process design for a solids-based CO_2 capture technology. The development of an effective, cost-efficient process faces multiple engineering challenges including: effective heat delivery to the sorbent regenerator, continuous movement of large quantities of sorbent, and a requirement to have reactor designs that provide sufficient gas-solid mass transfer.

Previous studies related to solid sorbent CO_2 capture have led RTI to consider a cyclic, thermalswing process design based on continuous sorbent circulation through dual fluidized, moving-bed reactors (FMBRs), for both the CO_2 sorption and desorption reactors. The proposed circulating, FMBR design concept not only meets all of the process requirements but also addresses the issues of scale and commercial availability of all process components. The MBS-based material, however, has only been developed in fixed-bed form and thus RTI and PSU are working to transition this sorbent into an attritionresistant, fluidizable form. In addition further engineering, design, and cost evaluations will be performed to further advance and prove the feasibility of this design choice. Ultimately, if the technology development is successful, RTI will lead an effort to design and fabricate a bench-scale continuous flow CO_2 capture prototype system. This system will be integrated and commissioned at a coal-fired power plant, where extensive parametric and long-term flue gas testing will be performed. It will also be tested using flue gas compositions that closely match those found in a typical NGCC plant.

3. Process Descriptions

3.1. Conventional MEA Based Solvent Capture Process

The process design for CO2 capture is based on the conventional MEA process without any process modifications as applied to the flue gas of a natural gas power plant[2]. The flue gas from the stack enters a direct contact cooler (DCC) at a high temperature and to be cooled down to lower temperatures for absorption. The cooled gas is fed into a blower (BLOWER) to account for the small pressure drop in the absorber. The compressed gas is fed into the MEA absorber with a counter-current stream of lean-MEA where CO_2 -rich stream of MEA exits the bottom of the absorber, and the vent gas is scrubbed for evaporated MEA upon which the vent gas is released into the atmosphere. The rich-MEA is then pumped through a cross heat exchanger where it is fed into the stripper, allowing high purity CO_2 to exit the top and a stream of lean-CO₂ MEA to be recycled back into the absorber. The high-purity CO_2 stream is then entered into a six-stage intercooling compression system where it is liquefied and pumped to pipeline specifications.

3.2. Solid Sorbent-Based Capture Process

A schematic of the solid based process for CO_2 capture from an NGCC power plant is shown in Fig. 1. In a similar manner to the MEA case, the NGCC flue gas is passed through a direct contact cooler for cooling to absorption temperature, and is then passed through a blower where the cooled gas is blown to the absorption unit. The absorption unit is designed and optimized to capture 90% of the CO_2 in the gas as in the conventional MEA solvent based plant. In the absorption unit, the gas enters the bottom of the absorber through a gas distributor, flows upward and is immediately contacted with the fluidized sorbent. As the fluidized sorbent reaches the bottom of the absorber, it is de-fluidized and is then mechanically conveyed to the regenerator. It is important to note that the mechanical conveying equipment will have an enclosure to minimize contact of the sorbent with the atmosphere. The sorbent enters the reactor where it is distributed across the unit's cross-sectional area and comes into contact with the power plant flue gas, which acts as the fluidizing gas. In the desorption unit, which has a similar design as the sorption unit, steam and CO_2 is fed to the bottom of the regenerator where it is used as a fluidizing gas and to provide some of the heat required for sorbent regeneration. The balance of the desorption heat is provided through condensing steam flowing through heat transfer internals within the regenerator. The regenerator is operated to regenerate 93% of the CO_2 in the sorbent (100% of the captured CO_2) by controlling the mass flow rate of the steam entering the unit. The regenerated sorbent then exits the bottom of the reactor and is again mechanically conveyed to the top of the absorber where it is reused for absorption. Prior to entering the sorption reactor, the hot sorbent coming from the regenerator can be run through a fluidizedbed heat transfer unit where some latent heat can be exchanged with the cooler sorbent leaving the sorption reactor – effectively pre-heating the CO_2 -rich sorbent prior to entering the regenerator. The CO_2 released from the sorbent exits the top of the regenerator where it is also sent to a six-stage intercooling compression system and exported to pipeline specifications.



Fig. 1 - Solid Sorbent Capture System Schematic

4. Process Simulations

4.1. Simulation Tools

The conventional MEA-based solvent process and the advanced sorbent based process were designed and modeled using the Aspen Plus 7.3 process simulation software. Aspen Plus is an ideal choice for the simulation due to its excellent property databanks that are needed to model all thermodynamic interactions between the CO_2 and the solvent. The sizing and costing of the equipment in the conventional process was done through the classical approach and will be explained in later sections. For the solidbased process, Aspen Process Economic Analyzer will be used to do the sizing and costing of the process equipment due to its seamless interfacing with the Aspen Plus modeling software.

4.2. Flue Gas Specifications, Direct Contact Cooler and Blower

The flue gas used in the process simulation is flue gas emitted from a model NGCC power plant specified as part of the United States Department of Energy's (DOE) Fossil Energy Innovations for Existing Plants (IEP) Program. [10]. The specifications of the flue gas (composition, flow rate, temperature and pressure) are included in Table 1 below. It is important to note that this report is used to ensure that a good baseline is used for the techno-economic evaluations for the NGCC case.

Parameters	Units	Values
Flue Gas Temperature	°C	106
Flue Gas Pressure	MPa	0.1
Flue Gas Flow Rate	kmol/hr	113381
Flue Gas Composition	mol%	
CO_2		4.04
H_2O		8.67
N_2		74.32
O_2		12.09
Ar		0.88

Table 1 - Flue Gas Specifications

The flue gas temperature is too high for absorption conditions in both processes and as a result, the gas needs to be cooled down (for both processes, the required temperature is 40° C). The gas is fed to the bottom of a direct contact cooling tower (DCC), rises and is contacted with cooling water to reduce the temperature to the desired temperature. The cooling water enters the top of the DCC at 30° C and exits the bottom where it is cooled and recycled back into the tower. The cooling is done across a heat-exchanger that feeds cooling water from the power (16° C, ambient pressure). The cooled flue gas exits the top of the DCC unit where it is fed into a blower prior to being sent to absorption.

The purpose of the blower is to increase the pressure of the cooled gas to a point where it can overcome the pressure drop that occurs in the capture units. We see that for:

- 1. The conventional process, the pressure drop occurs across the absorber. Literature values show that it falls within the range of 100mbar[11]. This is the value used in the process simulation.
- 2. For the solid process, the absorber is designed and operated such that the pressure drop across it is limited to 130mbar. This is the value used in the solid case simulation.

4.3. Conventional Process Simulation

The flue gas exiting the blower enters the bottom of the absorber at 1.1bar with a temperature of 49.8°C. Lean-MEA that is recycled from the stripper enters the top of the absorber (lean loading = 0.25, 40° C and ambient pressure) to capture 90% of the CO₂ contained in the flue gas. The absorber is modeled a three-equilibrium stages, with no condenser or reboiler. Absorption occurs best between 40-60°C and therefore the conditions in the absorber are favorable for the forward chemical absorption reaction. Remaining flue gas continues to the top of the absorber where it is washed down with water to capture any volatilized MEA as the result of the exothermic reaction. The remaining flue gas is then vented to the atmosphere. The CO₂ rich solvent is then pumped to a shell-tube exchanger prior to entering the stripper.

The rich-MEA stream needs to enter the stripper at a temperature and pressure favoring the reverse reaction to occur so that the CO_2 can be stripped and released for compression. The stream is thus sent to a shell-tube heat exchanger where the cold rich stream is heated to a temperature of 107°C using the lean-MEA stream recycled from the stripper back to the absorber. The heat exchanger is converged with a 5°C temperature approach, and the rich stream finally enters in the stripper. In the stripper, low pressure steam

from the power plant is passed through the reboiler to provide the proper environment for the CO_2 to be stripped. The unit is modeled as an 8 stage, equilibrium model with a reboiler and condenser (the condenser is set at 40°C). From the simulation, we see that the heat duty required to regenerate the solvent and release the CO_2 is 4.14GJ/tonne CO_2 , which for NGCC power plants is in agreement with previous works [11].



Fig. 2 - Six Stage Compression System

The pure CO_2 exits the condenser and enters a six-stage compression system with intercooling. A schematic of the compression system is shown in Fig. 2 The pipeline specifications required for compression are specified as 150bar and 35°C. The temperature is high to avoid any pipeline problems that may result when the liquefied product is being sent to the injection site. The compression stage profile and pressure drop in each stage is shown in Table 2 below.

Stage	Unit	Outlet Pressure (bar)
1	Compressor	3.59
2	Compressor	7.79
3	Compressor	17.10
4	Compressor	37.58
5	Compressor	82.74
6	Pump	152.72

Table 2 - Compression System Pressure Profile

5. Costing Methodology and Calculations

5.1. Costing Methodology and Economic Assumptions

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After sizing the equipment, the pure equipment cost (as in the cost of equipment without installation costs) is obtained directly from literature costing correlations [12–14] (for the conventional case) or from Aspen PEA (for the solid case). It has been agreed that equipment will be manufactured from stainless steel for the conventional case (this includes pumps, compressors, heat exchangers and tower units). Upon

that, a bare erect cost is totaled by adding the installation costs to the pure equipment cost. Installation costs are also obtained from literature.[13] Contingency fees are added to the bare erect cost to obtain a Total Plant Cost. Additional costs known as owner costs are added to the Total Plant Cost to obtain a Total Overnight Cost. The following assumptions are made for capital cost estimation[10]:

- 1. For the conventional case, process contingency is set to zero since most capture technologies are already proven. There is an added value of 20% for the process contingency for the solid case as it is still considered an unproven technology.
- 2. Project contingencies are calculated as 20% of the total of the bare erect cost and process contingency for both technologies.
- 3. Owner costs represent preproduction costs, working capital costs and financial costs required to fund this capital. Preproduction or startup costs include 6 months operating labor, 1 month maintenance material at full capacity, 1 month non-fuel consumables at full capacity, 25% of one month's fuel cost at full capacity, and 2% of Total Plant Cost. Working capital costs include inventory capital and the cost of land. For the inventory capital, the charges are 0.5% of Total Plant Cost for spare parts, a 60 day supply of fuel and non-fuel consumables at full capacity, and land for the NGCC case is 1000 acres charged at \$3000/acre.

Totaling these charges gives us the Total Owner's cost which is used in the calculation of cost of electricity (COE). The annual operating cost (OPEX) associated with the capture plant is calculated by determining its two components; the fixed operating cost and the variable operating cost. Fixed operating cost is the annual cost of labor associated with the plant, and the variable operating cost is in the form of maintenance materials, consumables and fuel associated with the plant. Fixed operating cost is calculated at full capacity while the variable operating cost is calculated at capacity factor of 0.85 (the capacity factor represents the fraction of time the plant is in operation throughout the year). The following assumptions are made for the operating costs[10]:

- 1. The average base labor rate is \$34.65/hr. The burden on this labor is charged as an additional 30% of the above rate. Administrative and support labor is charged as 25% of the labor burden.
- 2. Maintenance material costs are a function of the Total Plant Cost.
- 3. Taxes and insurance are set at a fixed 2% of the Total Plant Cost.
- 4. Consumables include water, chemicals and fuel used in the plant. These chemicals include solvent/sorbent, activated carbon and corrosion inhibitor used in the plant.

5.2. COE Calculation

The calculation of cost of electricity is usually done by performing a discounted cash flow analysis and determining the cost of electricity at which the net present value is zero by taking certain assumptions into account (taxes, discount rate, time analysis period, discount period). A simplified method for calculating the COE based on the costing assumptions [10]:

Cost of Electricity =
$$\frac{(CCF)(TOC) + OC_{FIX} + (CF)(OC_{VAR})}{(CF)(MWH)}$$
(1)
Where CCF = capacity charge factor (for NGCC power plant = 0.105, for NGCC with capture
= 0.111)
TOC = Total Overnight Cost
OC_{Fix} = Total Fixed Operating Cost
CF = Capacity Factor (as mentioned = 0.85)
(1)

OC_{Var} = Total Variable Operating Cost at 100% full capacity

MWH = Total annual power generated in megawatt hours at 100% full capacity

6. Results and Discussion

The result of the economic evaluation for the conventional MEA case is shown in Table 3. The cost of electricity without capture is \$58.7/MWh and after integrating the capture process, the cost rises to \$84.0/MWh. This represents an 84% increase in cost of electricity. Initial results for the solid sorbent CO_2 capture technology applied at a coal plant show that the total annual cost of capturing 3,476,848 ton- CO_2/yr , (equivalent to 90% CO_2 capture from a 550 MW coal power plant) was estimated to be a CO_2 captured cost of \$35 to \$45 per ton of CO_2 (a 28% increase in cost of electricity). By comparison, implementing the MEA solvent process for CO_2 capture results in CO_2 captured cost of \$68 per ton of CO_2 . It is expected that a similar economic benefit of the solid sorbent case would be present for the NGCC case. In the solid sorbent CO_2 capture case, initially we have identified the major contributors to the CO_2 capture cost are utility requirements, the capital charge, and CO_2 transportation, storage, and monitoring.

A detailed sensitivity analysis will be conducted to gauge how critical certain assumptions are to precisely predicting the cost of the advanced sorbent CO_2 capture process. A short list of these parameters is provided below. The existing research plan will be tailored to enable the verification of the assumptions made for the most critical parameters identified during the sensitivity analyses.

Table 3 -	NGCC	Conventional	Cost	Economic	Results
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Costs	Power Plant	Combined Cost
CCF	0.105	0.111
TOC (\$)	398,290,000	771,663,763
OC _{Fix} (\$)	12,247,740	19,961,619
CF	0.85	0.85
OC _{Var} (\$)	222,005,560	225,588,121
MW	555	475
MWH	4,862,501	4,164,278
COE (\$/MWh)	58.7	84.0

The parameters to be tested in the sensitivity analysis are:

- 1. The sorbent loss rate, capacity and price.
- 2. The impact of sulphur and nitrogen on sorbent performance.
- 3. The effect of heat of absorption and regeneration reactions.
- 4. The stripping steam demand.
- 5. The design of the reactor based on an equilibrium-limited kinetic model.

7. Conclusions

The MEA solvent based post combustion capture technology is difficult to implement commercially due to high parasitic power losses and the increase in cost of electricity. The solid based process proposed above is believed to be able to adhere to the aggressive performance targets set by the US DOE. Preliminary work on simulating the sorbent process for natural gas combined cycles is underway however initial work of simulating the process for a model coal case power plant show promise in reducing the cost of electricity and a similar benefit is expected to be realized for the NGCC application.

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