Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 1 (2009) 4047–4053

Energy Procedia

www.elsevier.com/locate/procedia

GHGT-9

Dynamic operation of amine scrubbing in response to electricity demand and pricing

Sepideh Ziaii[a], Stuart Cohen[b], Gary T. Rochelle[a,]*, Thomas F. Edgar[a], Michael E. Webber[b]

[a]Chemical Engineering Department, University of Texas, Austin, Texas 78712, USA
[b]Mechanical Engineering Department, University of Texas, Austin, Texas 78712, USA

Abstract

This paper examines dynamic operation of CO_2 capture with absorption/stripping using 7 m MEA, where the absorber is operated at full capacity with the stripper at reduced load. Depending on the cost of CO_2 emissions, doing so in response to variations in electricity demand could improve annual profits by \$10-\$100 million or more at facilities with CO_2 capture. Dynamic scenarios were simulated with a controlled, constant ratio of heat rate and solvent rate. With an 80% load reduction, scenarios that turn CO_2 capture off and on affect stripper performance only slightly and reach the steady state in about 90 and 18 minutes respectively.

Keywords: CO_2 capture; dynamics; modeling; absorption; stripping; flexibility

---

1. Introduction

Most analyses of CO_2 capture systems assume continuous operation at a full-load operating condition where the energy requirement for CO_2 capture and associated electricity production costs remain constant over plant lifetime. For a coal-fired power plant using post-combustion amine absorption/stripping for CO_2 removal, full-load CO_2 capture could reduce net energy output by 11-40% from that of an equivalent gross size plant without CO_2 capture [1, 2]. The bulk of this energy requirement is a consequence of the heat used for solvent regeneration and the work required to compress CO_2 to pipeline pressures for transport to a storage site. In a typical design, about 50% of the steam is extracted between the intermediate and low-pressure turbines, expanded in a let-down turbine that runs the CO_2 compression train, and then sent to the stripper column for solvent regeneration (see Figure 3) [3]. The resulting increase in production costs, coupled with the high capital costs of CO_2 removal equipment, greatly hinder the economic viability of CO_2 capture.

In contrast to static analyses, this paper examines the process feasibility and electric grid implications of flexible CO_2 capture operation. A post-combustion system can be operated flexibly by redirecting some or all of the steam being used for CO_2 capture back to the low-pressure turbine in order to increase power output when desired. Doing so allows stripping and compression systems to operate at reduced load, and while additional CO_2 may be emitted during part or zero-load operation, sufficient solvent storage could allow continued CO_2 capture in the absorber [4].

Previous work has shown that by operating CO_2 capture at low or zero-load during annual peak electric grid demand, the need to spend billions of dollars of capital costs to replace the capacity lost to CO_2 capture energy requirements can be avoided. A

---

* Corresponding author. Tel.: +1-512-471-7230; fax: +1-512-471-7060.
E-mail address: gtr@che.utexas.edu.

doi:10.1016/j.egypro.2009.02.211

study of the Electric Reliability Council of Texas (ERCOT) electric grid finds that the infrequency of annual peak electricity demand allows these capital savings to be achieved with less than 100 hours of zero-load operation throughout an entire year, so that CO_2 reductions are near those achieved with continuous operation even if CO_2 is vented when it is not removed [5]. Flexible CO_2 capture could increase plant output range and improve the ability of a plant to perform profitable grid reliability services [4]. By giving a plant operator the option to choose a desired CO_2 capture operating condition based on current market conditions such as fuel prices, CO_2 prices, and electricity demand, flexible CO_2 capture can be utilized to operate more economically than if capture systems are restricted to continuous, full-load operation.

2. Modeling flexible CO_2 capture in the ERCOT electric grid

A model of the ERCOT electric grid was created using MATLAB software and used to investigate how flexible CO_2 capture in response to hourly variations in electricity demand will affect performance, economics, and CO_2 emissions at power plants running CO_2 capture and in the electric grid as a whole.

Historic load and electric grid conditions were used from 2006 to perform calculations for a one-year period. In 2006, installed capacity in ERCOT included about 20% coal, 72% natural gas, and 6% nuclear-based generation, with additional capacity from wind, hydroelectric, and other sources. Lower marginal electricity production costs allow coal and nuclear-based plants to operate at base load with natural gas-fired plants meeting most of the remainder of electricity demand [6].

For this study, post-combustion CO_2 capture was assumed to be installed on enough of ERCOT's coal plants for the average coal fleet emissions rate to decrease by roughly 50% if CO_2 capture is operated continuously at 100% load. This goal requires CO_2 capture on 8 of the 15 ERCOT coal-fired facilities and would allow the coal fleet emissions rate to approach that of typical natural gas-fired facilities. Plants were chosen based on the lowest sum of electricity production costs with CO_2 capture at 100% load plus the capital charges of any required CO_2 and sulfur dioxide (SO_2) removal equipment. In scenarios that allow flexibility, CO_2 capture may operate at 100% and 20% load, and performance at these operating points is defined using results from the dynamic process model described in Sections 4 and 5 of this paper. CO_2 that is not captured was assumed to be vented to the atmosphere. System response time was not included explicitly, but it was assumed that the results from one hour calculation intervals will approximate those found when considering the system response time calculated using the dynamic process model described later in this report. A more flexible CO_2 capture system may allow several possible operating points, but this study chooses 100% and 20% load to investigate operation between two extremes.

The model used a specified CO_2 price along with fuel costs and other operation and maintenance (O&M) costs to determine marginal costs of electricity production for each plant in dollars per Megawatt-hour. These costs were then used to create a dispatch order from which the model chooses to use plants from the least to most expensive until demand in a particular hour is met. To represent ERCOT's competitive market for electricity, the marginal cost of the final (and most expensive) plant dispatched in a given hour was assumed to set the electricity price in that hour, from which operating profits of all plants can then be calculated. Because capital charges do not factor directly into dispatch decisions, they were not included in marginal electricity production costs. Calculated plant generation is used to determine CO_2 emissions.

Though the model does not consider transmission constraints or any other technical limitations of plant dispatch, the basic representation of dispatch and the electricity market still provides an effective framework to analyze the effects of flexible CO_2 capture on an electric grid.

The following scenarios are considered.

(1) *BAU*: The business as usual scenario considers the actual ERCOT grid in 2006 without any CO_2 capture.
(2) *CCS Base*: For the base case CO_2 capture scenario, CO_2 capture systems are operated at 100% load continuously throughout the year.
(3) *FLEX Op Costs*: In this flexible scenario, plants with CO_2 capture choose the operating condition (20% or 100% load) that has the lowest marginal costs of electricity production. When there is no cost of emitting CO_2, it will always be least expensive to operate at 20% load, and increasing the CO_2 price will eventually allow lower production costs at 100% load.
(4) *FLEX Profit*: This flexible scenario operates under the assumption of perfect knowledge of electricity demand and dispatch ordering prior to deciding whether to operate CO_2 capture at 20% or 100% load. In every hour, each plant with CO_2 capture calculates its hourly profits for two scenarios: if all plants with CO_2 capture operate at (A) 100% load or (B) 20% load. If profits are greater for a particular plant for Option A, that plant will operate capture at 100% load; otherwise, it will operate at 20% load. Because the output capacity of plants with CO_2 capture is lower at 100% load, Option A is likely to have a higher electricity price.

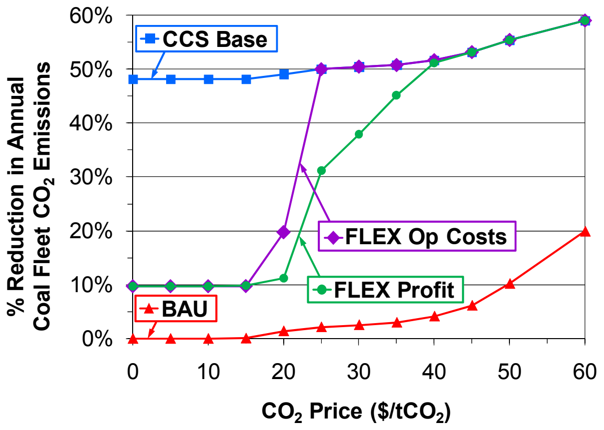

Figure 1: Reductions in annual CO_2 emissions in the ERCOT coal fleet in each scenario vs. CO_2 price

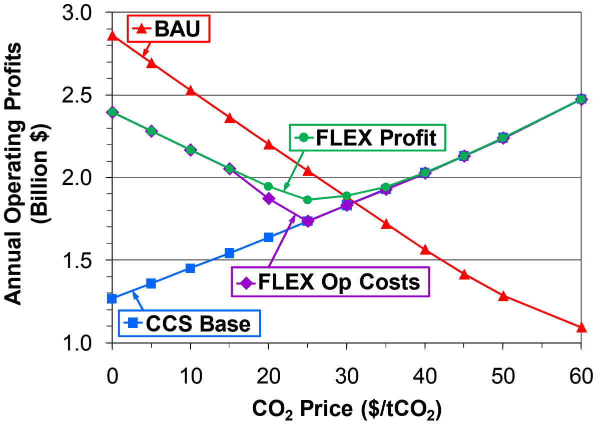

Figure 2: Cumulative annual operating profits in each scenario vs. CO_2 price at the eight coal-fired plants that use CO_2 capture (except in the *BAU* scenario)

3. Results and discussion of the implications of flexible CO_2 capture in ERCOT

Figure 1 displays the reduction in annual coal fleet CO_2 emissions for each scenario with CO_2 prices ranging from \$0-\$60/tCO_2 (2006 US\$ per metric ton of CO_2 emitted), with percent reduction calculated relative to emissions levels in the *BAU* case with no CO_2 price. Because electricity demand is assumed to be constant across all cases, changes in generation by plant type can be inferred from this figure. Emissions in the *BAU* scenario fall negligibly below \$15/tCO_2, less than 5% below \$40/tCO_2, and begin to decrease significantly at higher CO_2 prices. Coal-fired plants constitute a relatively small proportion of the ERCOT fleet, so CO_2 price must be relatively high before the added emissions costs at coal-based plants move them late enough in the dispatch order to be replaced by natural gas-fired facilities for base load generation. In all scenarios, any reduction in coal-based generation must be met by an equal increase in natural gas-fired generation, partially offsetting coal fleet emissions reductions. However, because natural gas emissions rates are roughly half that of coal without CO_2 capture, net electric grid emissions reductions on a percent basis are at least half of those calculated in the coal fleet.

CCS Base nearly achieves the desired 50% reduction in coal fleet CO_2 emissions at low CO_2 prices, and higher CO_2 prices allow further reductions as fuel switching begins to limit the output of coal-fired plants that do not use CO_2 capture. *FLEX Op Costs* begins with emissions reductions of about 10% at low CO_2 prices (when all CO_2 capture systems operate at 20% load), jumps to 20% when the two most efficient plants with CO_2 capture are less expensive to operate at 100% load, and then follows the *CCS Base* curve (when all CO_2 capture is at 100% load) above \$25/tCO_2. In contrast to plant economic studies that find the CO_2 price for economic viability of CO_2 capture to be around \$40/tCO_2, these data indicate that once a CO_2 capture system is built, the CO_2 price to justify 100% load operation may be closer to \$20-\$25/tCO_2 [7]. *FLEX Profit* requires CO_2 prices of about \$40/tCO_2 before CO_2 systems remain at 100% load throughout the year, indicating that flexible operation could improve operating profits in the \$20-\$35/tCO_2 price range. If CO_2 is vented when CO_2 capture is at part-load, flexibility may prevent the emissions reductions that could be achieved with continuous full-load operation, but reductions are still significant as long as the CO_2 price is high enough for marginal costs to be lower at 100% load.

Figure 2 displays cumulative annual operating profits at the eight coal-fired facilities using CO_2 capture. When no CO_2 capture is available (*BAU*), operating profits fall dramatically as CO_2 price increases, though it takes a CO_2 price of about \$30/tCO_2 before it is more profitable to operate with CO_2 capture installed. Because lower emitting natural gas-fired plants continue to set electricity prices, electricity production costs at coal-fired plants without CO_2 capture increase faster than electricity prices for a given CO_2 price increase, resulting in rapid profit decline. Though *CCS Base* has lower profits than *BAU* below \$30/tCO_2, it exhibits the opposite trend because emissions rates at coal-based plants with CO_2 capture are less than those of natural gas-fired facilities. *FLEX Op Costs* demonstrates that choosing between 100% and 20% CO_2 capture load allows much greater operating profitability than continuous 100% operation when CO_2 prices are too low to justify the operating expense. In the \$20-\$35/tCO_2 range, *FLEX Profit* improves profitability over *FLEX Op Costs* by allowing generators to consider the balance between marginal costs, power output, and electricity price at a given electricity demand and choose to operate in the most profitable manner. At \$25/tCO_2, such behavior improves annual operating profits by \$130 million over those earned with continuous 100% load operation. Flexibility has no impact on operating profits above \$35/tCO_2 in this static CO_2 price analysis;

however, the value of flexibility is expected to be greater in a cap and trade regime where CO_2 prices could fluctuate between values that justify CO_2 capture operation and those that do not.

4. Dynamic modeling of CO_2 capture

The absorption/stripping system typically consists of two columns. In the absorber, which is operated at atmospheric pressure and 40-60°C, the flue gas from a coal-fired plant containing 10-12% CO_2 contacts with MEA, and CO_2 is absorbed into the solution by physical and chemical mechanisms. The rich solution coming out of the absorber, which typically has a loading of 0.4-0.5 moles of CO_2/mole MEA, is directed to the stripper, operating at 1.5-2 atm and 100-120°C. Water vapor accompanying CO_2 from the top of the stripper is then condensed and returned to the water wash section of the absorber. The hot lean solution exiting the stripper is cooled by the cold rich solution in a cross heat exchanger (5-10°C temperature approach) and is furthered cooled to 40°C before entering the absorber (see Figure 3).

Several existing steady state models for absorption/stripping process with alkanolamines aim to minimize the energy use for CO_2 capture. However, these models do not have the capability of predicting the effects of dynamic operation on the system. No previous work was found on dynamic modeling of the entire absorption/stripping system or the stripper alone. Kvamsdal *et al.* [8] have prepared a dynamic model of CO_2 absorption by MEA using gPROMS® and studied the dynamics of the absorber in response to the start-up and power plant load change scenarios. In order to predict the dynamic behavior of CO_2 capture in response to variations in electricity demand, an accurate dynamic model is required. For this study, a rigorous rate-based dynamic model of the stripper, using 30 wt % MEA, was created in Aspen Custom Modeler®.

4.1 Model Development

In the stripper, mass transfer and chemical reactions occurring in the liquid phase result in desorption of CO_2 from the rich solution. In the present study, the stripper is modeled by the rate-based approach based on film theory, and kinetics is simplified by considering two dominant equilibrium reactions.

$$MEACOO^{--} + MEA^{+} \leftrightarrow 2MEA + CO_2 \quad (1)$$

$$MEA^{+} + HCO_3^{-} \leftrightarrow H_2O + MEA + CO_2 \quad (2)$$

Table 1 provides an overview of the important parameters in the model, along with their sources and literature.

Table 1: important parameters used in the stripper model

Property	Source	Comments
Partial pressure of CO_2 Equilibrium constants Heat of desorption	electrolyte-NRTL model developed by Hilliard	Regressed the points from flash calculation in the Aspen Plus® model by Hilliard
Density and viscosity of loaded MEA	Weiland *et al.* [9]	
Heat capacity of loaded MEA	Hilliard [10]	
Diffusivity of CO_2 in loaded MEA	Versteeg *et al.* [11]	Based on the N_2O analogy and a Stoke-Einstein relation
Liquid hold up	Suess and Spiegel [12]	
Pressure drop across the packing	generalized pressure drop correlation of Kister *et al.* [13]	
Liquid and vapor mass transfer coefficients	Onda *et al.* [14]	

4.2 *Ratio-Control Dynamic Strategy*

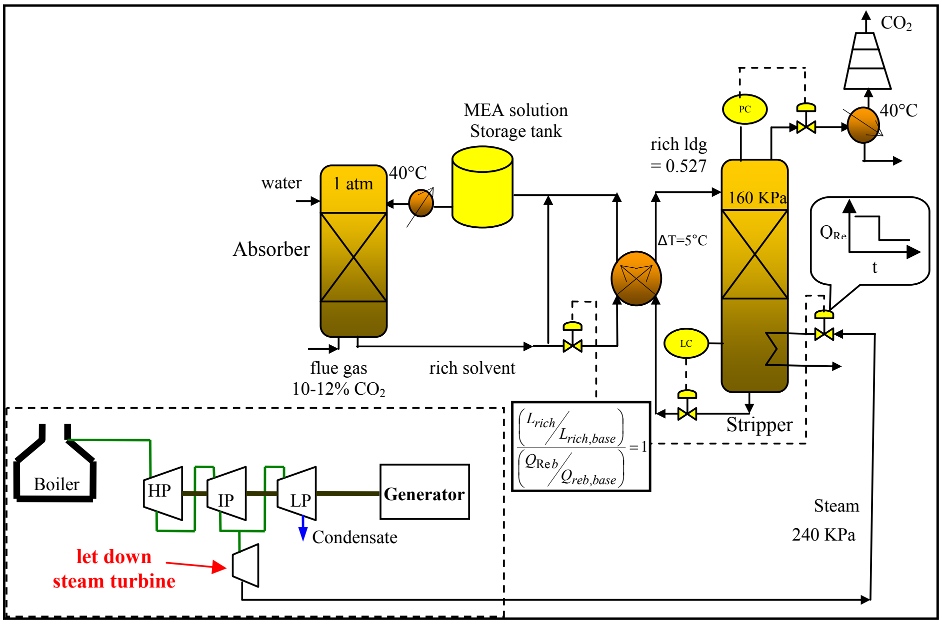

Figure 3: Steam turbines and CO_2 capture with ratio-control strategy

In this dynamic strategy, the absorber operates continuously, but the reboiler steam rate is reduced at the start of the peak period. Consequently, the absorber provides variable CO_2 removal. The non-regenerated rich solvent stream is mixed with the lean solution coming from the stripper and then returned to the absorber. In this option, no additional inventory is needed for rich and lean solvents, and the only input variable that significantly changes in the absorber is the lean loading. (Figure 3)

The following conditions are carried out for steady state design and dynamic simulation:

- CO_2 removal at 100% load: 90%
- Packing height: 2 m; column diameter: 4.6 m
- Overhead pressure is controlled at constant value (160 KPa).
- Liquid level in the reboiler is controlled at a constant level.
- The absorber is controlled such that it gives a constant rich loading in the presence of variable lean loading.

5. Dynamic simulation results and discussion

In order to demonstrate how the stripper responds to the flexible operation, two ratio-control scenarios are simulated:
1. Turn-off scenario: ramp the reboiler heat duty and rich solvent from 100% to 20% load in 15 minutes
2. Turn-on scenario: ramp the reboiler heat duty and rich solvent from 20% to 100% load in 15 minutes

In both cases, the simulation starts with 12 min at the initial load, and then the reboiler heat duty and rich solvent flow rate are ramped linearly to the desired final operating condition in 15 minutes. Figures 4 and 5 show the time response of reboiler temperature and lean loading in both dynamic scenarios. 100% load operation gives a larger pressure drop due to greater liquid and vapor rate and liquid hold up in the packing; consequently, with fixed pressure at top of the column, the reboiler would operate at higher pressure and temperature (see Figure 4).

The time response of the hydraulics of the column is related to the small liquid and vapor hold-up time in the packing. As can be seen in Figure 4, in the turn-off scenario, the liquid is initially cooled beyond the equilibrium point for 20% load because of the instantaneous flash in the simply modeled reboiler, and then the liquid temperature in the reboiler is further heated toward the steady state at the 20% load. This heating process is slow and most likely determined by the liquid hold-up in the reboiler. In the turn-on scenario, similar behavior is seen in the opposite direction.

Figure 5 reflects a very small change in the lean loading due to a change in load. The higher performance at 20% operation can be primarily attributed to the larger mass transfer unit, which is a factor of 1.7 greater than 100% load.

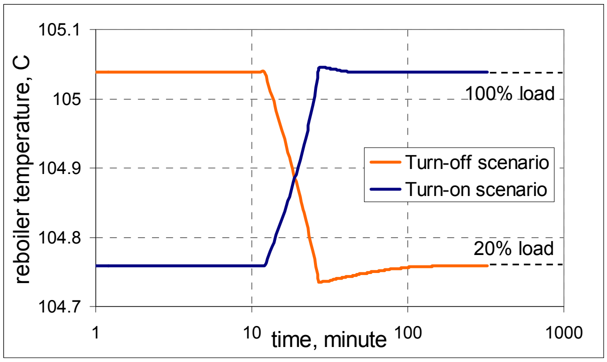

Figure 4: Dynamic responses of reboiler temperature to turn-on and turn-off operations

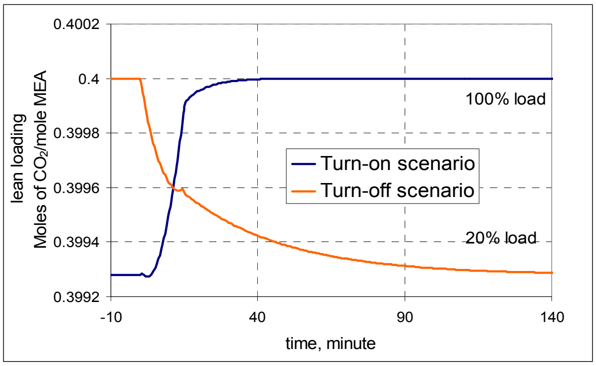

Figure 5: Dynamic responses of the lean loading to turn-on and turn-off operations

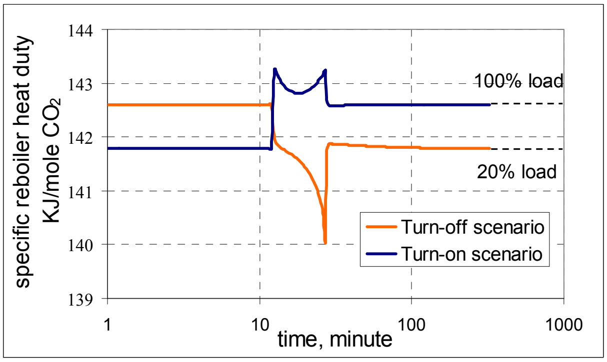

Figure 6: Specific reboiler heat duty calculated for the system operated in turn on and turn off operations

Figure 6 demonstrates how the calculated specific heat duty (KJ/mole CO_2) changes between 20% and 100% load operation. The specific heat duty, representing the performance of the stripper, does not vary significantly with the load. Although the transition curves show some discontinuities and irregular behavior, the temperature and lean loading response reflects smooth stripper behavior in response to the on/off operation. The initial and final step changes in the specific reboiler heat duty might be associated with the delay time in sensing change in the liquid rate in the reboiler. This kind of behavior might not be very realistic and could be eliminated or changed if the dynamics of the regulators of rich solvent and reboiler steam are coupled with the system.

The residence time of the liquid in the reboiler is the predominant factor influencing the response time of the stripper. The simulation shows that the liquid hold up in the reboiler achieves its final steady state value in just a few seconds after the final change is made to the solvent rate. Consequently, the average liquid residence time is very close to that of the final steady state. For this system, the liquid hold up time in the reboiler for 100% and 20% load operation is 5 and 25 minutes respectively. This effect is why turn-on operation reaches steady state approximately 5 times faster than turn-off operation.

In the current study, the overhead stripper pressure is kept constant and simplifying assumptions are made to the rich solvent conditions. In the future, the stripper model will be combined with an absorber model to evaluate the operational challenges in an integrated absorption/stripping system, and the current stripper model will be coupled with a CO_2 compressor model to study and compare the variable-pressure stripper in dynamic operation of CO_2 capture.

6. Conclusions

A basic model of the ERCOT electric grid is used to investigate the implications of flexible CO_2 capture in response to hourly electricity demand variations for a range of CO_2 prices. If CO_2 price is below that justified to operate CO_2 capture, flexibility may improve annual operating profits by hundreds of millions of dollars over those earned with continuous full-load operation, though CO_2 emissions will be greater if additional CO_2 is vented at part-load operation. Significant emissions reductions can be achieved with flexible operation when the CO_2 price is high enough for marginal costs of electricity production to be lower with full-load CO_2 capture. Above this CO_2 price, there is an additional range of CO_2 prices where flexibility can improve operating profits by tens or hundreds of millions of dollars above those received with constant 100% load operation by allowing plant operators to examine the balance among marginal costs, power output, and expected electricity price at different electricity market conditions and choose to operate CO_2 at the load that generates greatest operating profits in a particular hour.

Given these electric grid implications, the process feasibility of flexible CO_2 capture is examined using a rate-based dynamic model that is created in ACM® for the stripper using 30 wt % MEA. The model is capable of representing the dynamic behavior of the stripper column during the flexible operations. When ramping between 20% and 100% load over 15 minutes, the energy in KJ/mole CO_2 removed does not vary more than 2% during the transition. The 18-90 minutes response of flexible operations is determined by the solvent residence time in the reboiler at the end of the ramp.

7. Acknowledgments

This paper was prepared with the support of the Luminant Carbon Management Program, along with the Departments of Chemical and Mechanical Engineering at the University of Texas at Austin.

8. References

1. R.M. Davidson, Post-combustion carbon capture from coal fired plants – solvent scrubbing. IEA Clean Coal Centre. 2007.
2. J.A. Bergerson and L.B. Lave, Baseload Coal Investment Decisions under Uncertain Carbon Legislation. *Environ. Sci. Technol.*, 41 10 (2007) 3431-3436.
3. J.R. Gibbins, and R.I. Crane, Scope for reductions in the cost of CO_2 capture using flue gas scrubbing with amine solvents. *Proceedings of the Institution of Mechanical Engineers -- Part A -- Power & Energy* 218 4 (2004) 231-239.
4. H. Chalmers, J. Gibbins, and M. Leach, Initial Assessment of Flexibility of Pulverized Coal-Fired Power Plants with CO_2 Capture, in 3rd International Conference on Clean Coal Technologies for our Future, Sardinia, Italy, 2007.
5. S.M. Cohen, G.T. Rochelle, and M.E. Webber, Turning CO_2 Capture On & Off in Response to Electric Grid Demand: A Baseline Analysis of Emissions and Economics, in ASME 2nd International Conference on Energy Sustainability, Jacksonville, 2008.
6. ERCOT, 2006 Annual Report. 2006.
7. E.S. Rubin, C. Chen, and A.B. Rao, Cost and performance of fossil fuel power plants with CO_2 capture and storage. *Energy Policy*, 35 (2007) 4444-4454.
8. H.M. Kvamsdal, J.P. Jakobsen, K.A. Hoff, Dynamic Modeling and Simulation of a CO_2 Absorber Column for Post-Combustion CO_2 Capture, *Chem. Eng. Process*. (2008) doi:10.1016/j.cep.2008.03.002.
9. R.H. Weiland, J.C. Dingman, D.B. Cronin, G.J. Browning, Density and Viscosity of Some Partially Carbonated Aqueous Alkanolamine Solutions and Their Blends. *J. Chem. Eng. Data*, 43 (1998) 378-382.
10. M.D. Hilliard, Predictive Thermodynamic Model for an Aqueous Blend of Potassium Carbonate, Piperazine, and Monoethanolamine for carbon dioxide capture from flue gas. Ph.D. Dissertation, The University of Texas at Austin, Austin, TX., 1996.
11. G.F. Versteeg, L.A.J. van Dijck, W.P.M. van Swaaij, On the Kinetics Between CO_2 and Alkanolamines both in Aqueous and Non-aqueous Solutions. An Overview, *Chem. Eng. Commun*. 144 (1996) 113.
12. P. Suess and L. Spiegel, Hold-up of Mellapak Structured Packings. *Chem. Eng. Process.* 31 (1992) 119-124.
13. H.Z. Kister, J. Scherffius, K. Afshar, E. Abkar, Realistically Predict Capacity and Pressure Drop for Packed Column. AIChE meeting. Houston, TX, Spring, 2007.
14. K. Onda, H. Takeuchi, Y. Okumoto, Mass Transfer Coefficients between Gas and Liquid Phases in Packed Columns. *J. Chem. Eng. Jpn.* 1 (1968) 56-62.