

# **Carbon Capture Systems Analysis: Comparing Exergy Efficiency and Cost of Electricity of Existing and Future Technology Options (Progress Report 2014)**

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## **Abstract**

Given the likelihood that carbon-based fuels will continue to play a major role in electricity generation, carbon capture and storage systems will be a necessary part of future generating capacity. With this research project, we aim to develop a framework for quantitative evaluation of existing and proposed carbon-capture technologies. This framework is based on an exergy-based systems analysis performed at the local (system) level and at the global (life cycle) level, and a techno-economic evaluation of the technology.

At the system level, work to date has focused on three tasks, all related to adsorption-based systems: (1) the derivation of a thermodynamically rigorous definition of the exergy of any adsorbed mixture of species, including non-ideal mixtures that may include water; (2) building a set of property methods for adsorbed phases, so that thermodynamic information can be quickly accessed and used for modeling; and (3) performing an exergy analysis of a pressure swing adsorption system. At the life cycle level, work to date has focused on two tasks: (1) the development of custom-written Matlab code for exergetic life cycle calculations, using data from the *Ecoinvent Data v3* life cycle assessment database; and (2) applying this code to models of two fossil-fuel based power plants, with and without an amine absorption carbon capture system, to demonstrate the functionality of the code. Overall then, the work to date has involved building robust and re-usable tools to enable the local- and global-scale exergy analysis of carbon capture systems.

## **Introduction**

With this research project, we seek to answer the set of questions: What technologies or combination of technologies can provide CO<sub>2</sub> capture at energy costs much closer to underlying thermodynamic limits? Are the conditions and technology configurations required to achieve such efficiencies possible with available or foreseeable materials? What are the broader (i.e., full system) environmental implications of such technology implementations? What are the likely costs of these technologies? And, given all of the above considerations, which technologies are likely to supply practical, cost-competitive electricity with low life-cycle CO<sub>2</sub> emissions?

We are approaching these questions by focusing on four types of carbon capture and storage (CCS) systems with different characteristics, ensuring that a representative range of technologies are studied. Each of the four CCS technologies will be evaluated on three

bases: (1) an exergetic systems analysis so that the evaluation takes place with respect to absolute, thermodynamic limits; (2) a full life-cycle basis such that all ancillary exergy consumption and destruction—both embodied components and in-process interactions with the environment—are included; and (3) a techno-economic analysis of the technology such that technology options can be evaluated via economic metrics as well.

The systems include one baseline option—namely, a MEA/NGCC reference system such as the one studied by NETL [1]—for calibration of methodology, and three advanced technologies. The advanced technologies were chosen in conjunction with GCEP to represent the range of CCS options, and to complement the work of other GCEP research groups. They include one metal-organic framework (MOF) based adsorption system, one biomimetic sorbent, and one ionic liquids absorption system.

Our three-part analysis will result in three metrics for each system: work-specific exergy consumption, work-specific carbon emissions to the atmosphere, and first-order estimates of levelized cost of electricity (where the work is the output of the associated power plant, as reduced by the added carbon-capture system). Each of these metrics can be defined on a local (system-only) and global (life cycle) basis. In order to arrive at these metrics, we will be generating exergy distribution plots of each system. These are plots which show the magnitude of exergy destruction in each sub-process in the system, which can both help us understand the inherent inefficiencies in the system and, in the future, to target the most inefficient sub-systems for improvement. The end goal of this project is not only to provide accurate analyses of selected carbon-capture options, but to frame the comparisons of these options in a coherent, compelling way.

## **Background**

Despite growing concerns about climate change, it is very likely that carbon-based fuels will continue to be used in the coming decades for base-load power generation and for firming of intermittent renewable power sources. Carbon dioxide capture and storage (CCS) is therefore a necessary part of any comprehensive strategy for achieving required reductions in carbon emissions to the atmosphere. Significant studies of proposed carbon capture systems have been performed, including those produced as part of the IPCC process [2], those produced by the U.S. DOE [1], those from the IEA [3], and numerous academic and industrial analyses [4], [5], [6]. These studies arrive at the common conclusion that existing options for post-combustion carbon capture lead to a significant loss of plant output (as much as 30%) and a significant rise in cost of electricity (as much as 80%) when compared to a similar plant without carbon capture.

These numbers might be deemed acceptable—perhaps even unavoidable—were it not for the fact that thermodynamic limits suggest that much more efficient processes are possible. Considered in terms of the minimum work required to separate carbon dioxide generated by combustion of natural gas from its flue gas at atmospheric pressure, only a 2.4% loss of plant output is actually required [7]. Note that even after compressing the CO<sub>2</sub> to 100 bar (the pressure prescribed by NETL for use in comparing separation options, [1]), the fraction of exergy required has only risen to 3.5%. These figures

illustrate a key point: Assuming an exergy efficiency of  $\sim 50\%$ <sup>1</sup> for the overall plant, it should be possible to develop a separation methodology that meets NETL specifications while incurring only a 7% loss of plant output.

This leads to a need to analyze the performance of carbon capture systems via an exergy analysis, in order to compare their operation to this thermodynamic baseline. The objective of this type of analysis is to understand the distribution of exergy within a system such that the causes of its destruction are exposed and quantified. With the exergy distribution of a plant or process known, not only is its overall quality assessed with respect to a fundamental, absolute yardstick, but the locations and magnitudes of losses are revealed for inspection (and thereby improvement). Exergy analysis provides both an unambiguous assessment and immediately points the way to process improvement.

For two reasons, we chose to begin our systems analysis with an adsorption system. The first reason is that two of our advanced carbon capture systems are adsorption-based (the MOF system and the biomimetic sorbent system). The second reason, which became clearer as we advanced in the project, is that very little had been done previously in developing the tools necessary for performing exergy analyses of adsorption-based gas separation systems (whereas absorption-based systems have been studied more extensively). Therefore, our progress on this topic has consisted of two complementary efforts: the development of a generalized and thermodynamically rigorous understanding of the exergy of adsorbed species and mixtures, and the application of this new understanding to an adsorption system model for CO<sub>2</sub> capture from flue gas.

Our research takes the analysis beyond the local system level by incorporating global effects in the comparison of carbon capture systems. Using results from the exergetic systems analysis, we are conducting a life-cycle assessment (LCA) in order to better understand how a given CCS technology interacts with the environment at broad scales. This assessment includes not only direct energy consumption (i.e., exergy consumption) at a facility, but also the exergy destruction associated with all “embodied” materials and components, as well as the operational interactions with the environment. The goal of this analysis is to understand which technology option results in the smallest disruption to the environment and results in the smallest drawdown of valuable energy and material resources (e.g., exergy stores) across the entire supply chain. This will enable a better understanding of the tradeoffs between using sophisticated material inputs (which often require more embodied energy inputs) and reducing energy impacts on site.

A number of LCAs have been performed of CCS technologies [8], [9], [10]. These LCAs serve to situate a CCS technology within the broader industrial ecosystem, tracking all material and energy flows both upstream and downstream of a technology of interest. In our case, this set of material and energy flows is utilized in an exergetic approach to LCA [11], [12], [13]. Several professional LCA datasets exist, such as the GaBi databases or the U.S. LCI database. After an overview of the available options, we chose to purchase the *Ecoinvent Data* life cycle assessment database, commissioned by the Swiss Centre for Life Cycle Inventories. The selection was based largely on the

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<sup>1</sup> For example, the exergy efficiency of a modern (F-class) NGCC power plant is  $\sim 52\%$ .

accessible nature of the raw database files, from which we could construct and manipulate individual matrices and perform exergetic life-cycle assessments without the utilization of a third-party LCA software package.

## Results

### *Exergetic Systems Analysis: Exergy of Adsorbed Mixtures*

In order to perform a detailed exergy analysis of an adsorption-based carbon capture system, we needed to be able to define the exergy of adsorbed species. This required a firm grounding in the thermodynamics of adsorbed species and mixtures in general, and of adsorbed mixtures of CO<sub>2</sub>, N<sub>2</sub>, and water in particular. To our knowledge, the only previous attempt to characterize the exergy of adsorbed phases was done by Kearns and Webley in 2004 [14]. In their paper, they arrive at an expression for the exergy of a combined system of a binary gas mixture, a given mass of sorbent, and a binary adsorbed mixture in equilibrium with the gas phase. Although they did not do this, the exergy of the adsorbed phase alone could then be isolated by subtracting the exergy of the other parts of the system (the sorbent and the gas phase). The two key underlying assumptions in their derivation are (1) that the adsorbed species are at very low surface coverage, such that there is a linear relationship between gas phase pressure and the amount adsorbed, and (2) that all gases, both in the system and in the environment, behave as ideal gases with constant specific heats.

The first assumption is almost never valid for adsorption systems that separate CO<sub>2</sub> from N<sub>2</sub>; in most regions of interest, the CO<sub>2</sub> adsorption follows a Langmuir isotherm form, not a linear one. This tool, then, wasn't useful for evaluating carbon capture systems. The second assumption is often valid, but it isn't necessary—because exergy is a state property of a substance, we should be able to define it without needing to impose an equation of state on the environment outside the system. In keeping with our mission of providing a set of tools for evaluating any new adsorption-based carbon capture technology, we set out to derive an expression for the exergy of adsorbed phases that could be applied completely generally.

First, we solved for the maximum useful work possible if an adsorbed phase were to be equilibrated with the environment—i.e., we found the exergy of this phase—while imposing only that matter and energy must both be conserved, and that transfers of heat, work, and matter should all be allowed between the system and the environment during equilibration. We arrived at an expression that imposed no equation of state on any part of the system or environment, and is therefore completely general:

$$X^a = U^a - T_0 S^a - \Phi_0 - \sum_{i=1}^{species} \mu_{i,0} N_i^a, \quad (1)$$

where the superscript *a* refers to the adsorbed phase, the subscript *0* refers to the environmental state, *U* is the internal energy, *S* is the entropy, and *N<sub>i</sub>* is the amount (moles) of species *i* in the system. The quantity  $\Phi$ , which is known as the surface potential, is the change in the chemical potential of the clean sorbent surface that results from adsorbing species onto it (see [15], [16], among others). Those familiar with expressions for the exergy of bulk phases (as opposed to surface phases, which are treated here) may notice an apparently “missing” term: the product of the atmospheric

pressure and the system's volume ( $P_0V$ ). This term disappears over the course of the derivation due to the use of the Gibbs dividing surface to define the surface properties.

Then, we needed to understand how to define the entropy and internal energy of adsorbed mixtures, and the surface potential. For this, we drew heavily on the existing literature covering the thermodynamics of adsorbed phases, particularly the work that developed the Ideal (and the extension to non-ideal) Adsorbed Solution Theory. All thermodynamic properties of pure adsorbed species can be derived from the shape of the adsorption isotherm and by knowing that the chemical potential of gas and adsorbed phases are equal at equilibrium [17]. Making ideal mixtures from these pure species in a thermodynamically consistent way was laid out by Myers and Prausnitz [18], and the incorporation of adsorbed phase activity coefficients was elucidated by Siperstein and Myers [19].

Understanding how to calculate entropy and internal energy of adsorbed species was critical to calculating the exergy of these species. Understanding how to calculate entropy and internal energy of *mixed* adsorbed phases was critical to calculating the exergy of adsorbed mixtures (which are inherent in separation processes like carbon capture). And finally, while adsorbed mixtures of nitrogen and carbon dioxide are usually well-represented by an ideal mixing assumption, understanding how to calculate thermodynamic properties of *non-ideal* mixtures of adsorbed species can be important when one of those species is water, which often mixes non-ideally with non-polar species like CO<sub>2</sub> and N<sub>2</sub>.

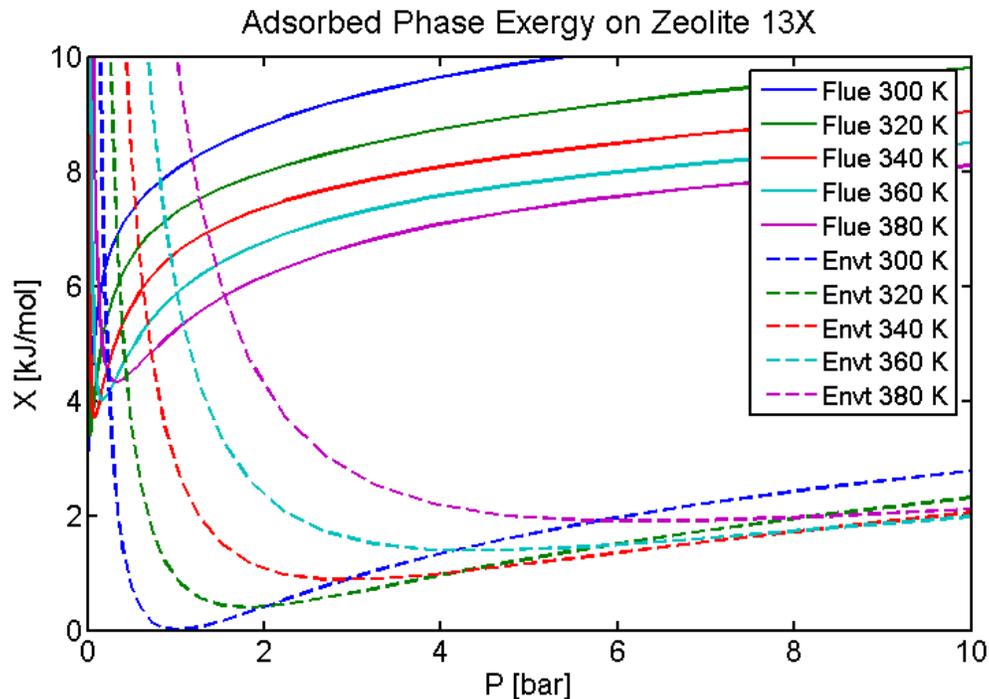
In short, we now have the ability to calculate the exergy of any adsorbed phase, in any adsorption-based system, including any used for carbon capture. As a confirmation, we are able to show that when Kearns and Webley's assumptions are applied (ideal gases with constant specific heats, low surface coverage of ideally-mixing adsorbed species), our expression reduces to theirs. The abstract for a paper presenting this work has been proposed to the next International Conference on Greenhouse Gas Technologies (GHGT-12).

#### *Exergetic Systems Analysis: Modeling*

Having developed a rigorous expression for the exergy of the adsorbed phase, we moved into the system modeling effort. First, we developed a set of functions in Matlab that would perform all the calculations necessary for finding the thermodynamic properties of an adsorbed phase, pure or mixed. This allows us to call the exergy, entropy, internal energy, and Gibbs and Helmholtz free energies of an adsorbed phase if given the state of the gas in equilibrium with it (currently, as set by the temperature, pressure, and mole fractions—although other formulations are certainly possible). This functionality is demonstrated in Fig. 1, which shows the exergy of two different adsorbed mixture compositions, as the system temperature and pressure are varied. These are functions that could be shared and re-used in future analyses of other systems.

We are now in the process of applying these functions to perform an exergy analysis of a vacuum-swing adsorption cycle for carbon capture. This work is being done collaboratively with Reza Haghpanah, who recently finished a post-doctoral fellowship in

the department of Energy Resources Engineering, and whose doctoral thesis focused on the modeling and optimization of adsorption systems for carbon capture [20]. This collaboration is interesting because the structure of his existing code for modeling a PSA cycle lends itself well to our purposes. Reaching cyclic steady state in these types of models is a computationally intensive process, and simplifications to the sorbent bed model (e.g., imposing isothermal conditions or neglecting pressure drops in the bed) are often made in order to speed up the modeling time. This code makes no such simplifications, which is important in order to correctly track the exergy flows and destructions. Furthermore, the code is tunable and can be run such that the column is discretized in 1D (which is faster computationally) or 2D (axially and radially, which is necessary when heat transfer to the environment is significant).



**Figure 1:** Exergy of two different mixtures adsorbed onto zeolite 13X. The first has adsorbed from flue gas (15%mol CO<sub>2</sub> in the gas phase); the second has adsorbed from the dead state, or environmental state. Note that zero exergy is reached at the environmental composition, environmental pressure (1 bar), and environmental temperature (300 K).

We have built and tested code that has the ability to perform an exergy analysis of the column based on the PSA cycle model's results. Interfacing the two sets of code—the exergy analysis section and the PSA cycle model section—is underway. As the interfacing has progressed, we have been developing a set of modeling criteria that must be met if an adsorption cycle model is to be used to draw conclusions about the exergy efficiency of the system. To date, this has included:

- the need for much tighter tolerances on energy and matter balances than are often allowed in discretized models of sorbent columns. The fact that exergy destruction is a closure term on the exergy balance equation means that even

small errors in matter and energy balances can have an outsized effect on the resulting exergy destruction term, leading to nonsensical results.

- the need to represent the adsorption of mixtures in a thermodynamically consistent way. This precludes the use of certain forms of adsorption isotherms, including some commonly used ones.

When our model integration is complete, we will therefore be able not only to provide insight into the exergy destruction mechanisms in adsorption-based carbon capture systems, but also to inform the future work of other researchers interested in performing similar analyses.

### *Exergetic Life-Cycle Analysis*

A primary goal of this project is a full life-cycle assessment of four carbon-capture technologies, focused on the exergy destruction associated with each technology. This assessment includes not only direct exergy consumption at a facility, but also the exergy destruction associated with all “embodied” materials and components, as well as the operational interactions with the environment. The goal of this analysis is to understand which technology option results in the smallest disruption to the environment and results in the smallest drawdown of valuable energy and material resources (i.e., exergy stores) across the entire supply chain. This will enable a better understanding of the tradeoffs between using sophisticated material inputs (which often require more embodied energy inputs) and reducing energy impacts on site.

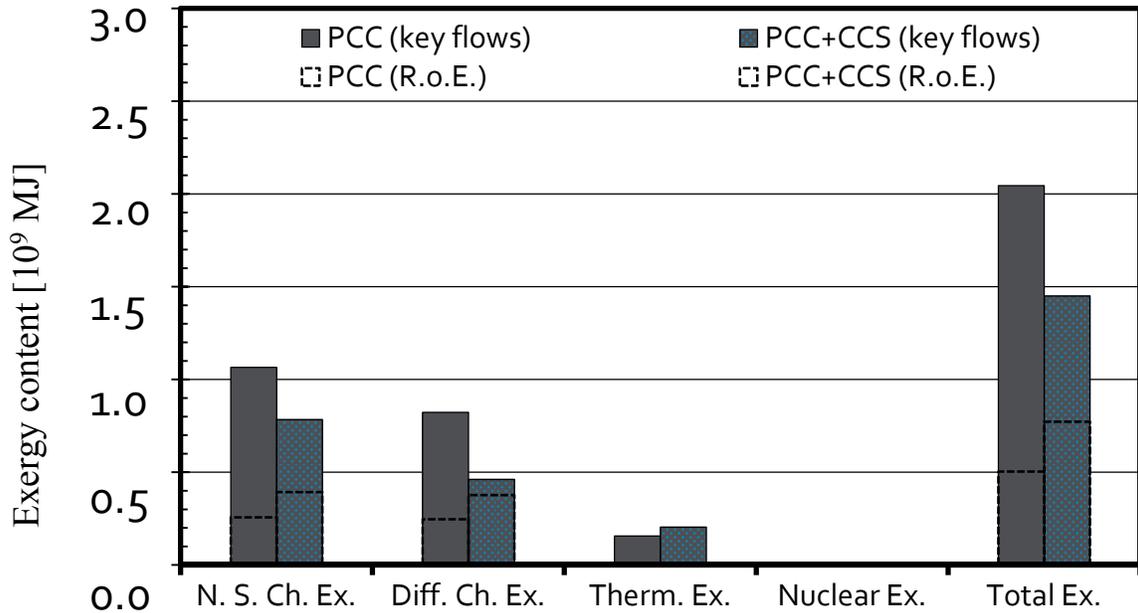
Work on this exergetic life-cycle analysis of CCS systems has progressed out of the initial planning and conceptualization stage, and a preliminary analysis has been performed. Methodologies for performing the life-cycle assessment, and more importantly the conversion of LCA results into an exergetic impact valuation, have been codified and implemented. Purpose-built code has been written for the creation of both ‘technology’ and ‘intervention’ matrices from the raw *Ecoinvent* v.3 dataset. These matrices represent the interactions of all technologies within the ‘technosphere’ (all human technological processes) and the interactions of these technologies with the environment. Additional code has been developed to perform matrix-based LCA calculations, and to convert the resulting environmental intervention vectors from collections of mass flow to the corresponding flows of exergy.

Using technology [**A**] and intervention [**B**] matrices compiled from the raw *Ecoinvent* database, a trial LCA was performed of the form:

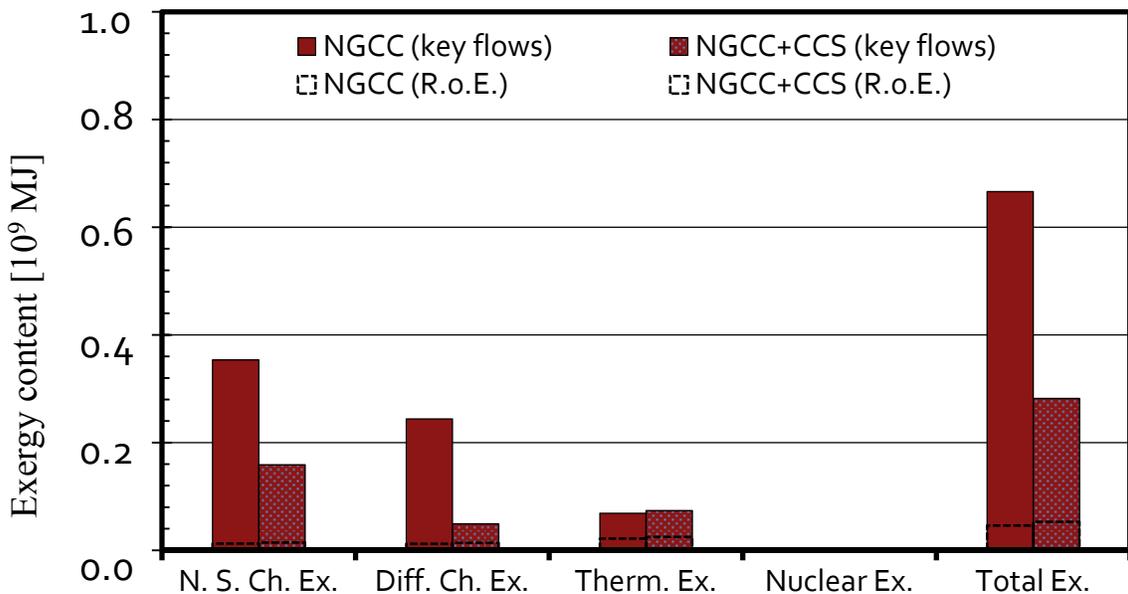
$$\mathbf{g} = (\mathbf{B} \mathbf{A}^{-1}) \mathbf{f} \quad (2)$$

where  $\mathbf{f}$  is a final demand vector, and  $\mathbf{g}$  is the resultant environmental inventory vector created during the production of  $\mathbf{f}$ . The  $\mathbf{f}$  vectors modeled in our preliminary exergy analysis comprised two electricity generation technologies, pulverized coal combustion and natural gas combined cycle, each with and without an attached post-combustion carbon capture and sequestration facility (specifically a monoethanolamine based absorption column).

Depositional exergy flows take the form of normal standard chemical exergy, diffusive chemical exergy, thermomechanical exergy, and nuclear exergy. Preliminary atmospheric contributions to exergy deposition in the natural environment from both PCC and NGCC generation are detailed in Fig. 2.



**Figure 2a:** Full life cycle exergetic deposition to air as a result of the generation of  $4.56 \times 10^9$  MJ of high voltage electricity from a pulverized coal combustion plant.



**Figure 2b:** Full life cycle exergetic deposition to air as a result of the generation of  $4.56 \times 10^9$  MJ of high voltage electricity from a natural gas combined cycle plant.

These plots show the exergy destruction in the atmosphere as a result of the construction and operation of each of the four types of power plant (NGCC, PCC, with/without CCS). What these preliminary results indicate is that, across the entire life cycle of the plant, the PCC plant with no carbon capture results in the greatest exergy destruction per unit of electricity generated, followed by the PCC plant with CCS, the NGCC with no CCS, and finally the NGCC with CCS." Current work involves refining the final demand vector to more accurately model a post combustion CCS facility's construction and operation, with the goal of performing a comparative analysis of several proposed cutting edge CCS technologies.

### **Progress**

The project has progressed on several fronts. Our systems analysis effort has focused on developing the tools necessary for performing exergy analyses of adsorption-based carbon capture systems, because that is where we felt the most work was needed. At this point, we have the ability—both theoretically and in a set of property methods built in Matlab—to calculate the exergy of any adsorbed phase, in any adsorption-based system, including any used for carbon capture. We are in the process of applying this set of adsorbed phase property methods to the exergy analysis of a pressure swing adsorption system.

Our efforts on the topic of exergetic life cycle assessment of carbon capture technologies have, similarly, focused on developing the tools necessary to track the exergy destruction in carbon capture systems on a global scale. This has involved writing custom code to extract life cycle data from the *Ecoinvent* commercial database and to manipulate this data to return the flows of exergy to and from the environment. This code has been applied to perform a preliminary exergetic life cycle analysis of NGCC and PCC power plants, with and without an amine-absorption carbon capture system.

Overall then, the work to date has involved building robust tools to enable the local- and global-scale exergy analysis of carbon capture systems, and by doing so, to provide a framework for evaluation and comparison of new and existing carbon capture technologies.

### **Future Plans**

The immediate future plans of the systems analysis effort are to complete the exergy analysis of a representative pressure swing adsorption system for carbon capture. After this is completed, a reference MEA-based system will be modeled in Aspen Plus, in order to provide a baseline against which to compare the adsorption system. The “novel” absorption system (ionic liquids) is expected to be able to be built and analyzed from modifications to the MEA system.

The immediate future plans of the life cycle assessment effort are to refine the final demand vector from the preliminary results shown here, to more accurately model the construction and operation of an MEA-based capture system. After this is completed, the newly-built tools will be applied to the analysis of the novel adsorption and absorption systems.

## References

- [1] J. Black, Cost and Performance Baseline for Fossil Energy Plants: Volume 1 - Bituminous Coal and Natural Gas to Electricity (Revision 2), Pittsburgh, PA: National Energy Technology Laboratory (NETL), 2010.
- [2] IPCC, Special Report on Carbon Dioxide Capture and Storage, Cambridge, UK: Cambridge University Press, 2005.
- [3] J. Davison, "Performance and costs of power plants with capture and storage of CO<sub>2</sub>," *Energy*, vol. 32, no. 7, pp. 1163-1176, 2007.
- [4] E. S. Rubin, C. Chen and A. B. Rao, "Cost and performance of fossil fuel power plants with CO<sub>2</sub> capture and storage," *Energy Policy*, vol. 35, no. 9, pp. 4444-4454, 2007.
- [5] H. Herzog, J. Meldon and A. Hatton, "Advanced post-combustion CO<sub>2</sub> capture," *Clean Air Task Force*, 2009.
- [6] W. Hermann, "An assessment of carbon capture technology and research opportunities," Stanford, CA: Global Climate & Energy Project, 2005.
- [7] C. F. Edwards, "Exergy Revisited," in *Course Notes for ME370B*, Stanford, CA, Stanford University, Department of Mechanical Engineering, 2012.
- [8] M. Pehnt and J. Henkel, "Life cycle assessment of carbon dioxide capture and storage from lignite power plants," *International Journal of Greenhouse Gas Control*, vol. 3, no. 1, pp. 49-66, 2009.
- [9] N. A. Odeh and T. T. Cockerill, "Life cycle GHG assessment of fossil fuel power plants with carbon capture and storage," *Energy Policy*, vol. 36, no. 1, pp. 367-380, 2008.
- [10] J. Koornneef and e. al., "Life cycle assessment of a pulverized coal power plant with post-combustion capture, transport, and storage of CO<sub>2</sub>," *International Journal of Greenhouse Gas Control*, vol. 2, no. 4, pp. 448-467, 2008.
- [11] G. Finnveden and P. Östlund, "Exergies of natural resources in life-cycle assessment and other applications," *Energy*, vol. 22, no. 9, pp. 923-931, 1997.
- [12] J. Dewulf et al., "Cumulative Exergy Extraction from the Natural Environment (CEENE): a comprehensive Life Cycle Impact Assessment method for resource accounting," *Environmental Science & Technology*, vol. 41, no. 24, pp. 8477-8483, 2007.
- [13] M. Bosch et al., "Applying cumulative exergy demand (CExD) indicators to the Ecoinvent database," *The International Journal of Life Cycle Assessment*, vol. 12, no. 3, pp. 181-190, 2007.
- [14] D. T. Kearns and P. A. Webley, "Application of an adsorption non-flow exergy function to an exergy analysis of a pressure swing adsorption cycle," *Chemical Engineering Science*, vol. 59, no. 17, pp. 3537-3557, 2004.
- [15] D. M. Ruthven, Principles of Adsorption and Adsorption Processes, New York: John Wiley and Sons, 1984.
- [16] D. P. Valenzuela and A. L. Myers, Adsorption Equilibrium Data Handbook, Prentice Hall, 1989.

- [17] A. L. Myers, "Thermodynamics of adsorption in porous materials," *AIChE Journal*, vol. 48, no. 1, pp. 145-160, 2002.
- [18] A. L. Myers and J. M. Prausnitz, "Thermodynamics of mixed-gas adsorption," *AIChE Journal*, vol. 11, no. 1, pp. 121-127, 1965.
- [19] F. R. Siperstein and A. L. Myers, "Mixed-gas adsorption," *AIChE*, vol. 47, no. 5, pp. 1141-1159, 2001.
- [20] R. Haghpanah et al., "Multiobjective optimization of a four-step adsorption process for postcombustion CO<sub>2</sub> capture via finite volume simulation," *Industrial & Engineering Chemistry Research*, vol. 52, pp. 4249-4265, 2013.

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