Carbon Capture Systems Analysis: Comparing Exergy Efficiency and Cost of Electricity of Existing and Future Technology Options (Progress Report 2013)

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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. Work to date has focused on two tasks: (1) the development of a system model for a generalized adsorption unit using custom-written code in Matlab, after surveying available commercial flowsheeting software; and (2) the development of custom-written Matlab code for exergetic life cycle calculations, using data from the *Ecoinvent Data v2.1 (2009)* life cycle assessment database.

Introduction

With this research project, we seek to answer the set of questions: What technologies or combination of technologies can provide CO_2 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 (e.g., 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_2 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. 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. We believe that our three metrics will allow such a comparative analysis.

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 [4-6]. 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_2 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 ~50%[1] 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.

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[1] For example, the exergy efficiency of a modern (F-class) NGCC power plant is ~52%.

Our research takes the analysis further by incorporating global effects in the comparison of carbon capture systems. Using results from the exergetic systems analysis, a life-cycle assessment (LCA) will be conducted 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 [8-10]. 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 will be utilized in an exergetic approach to LCA [11-13].

Results
The project is still in its early stages, having begun recently. To date, work has focused on two tasks: developing the model for an adsorption system on the exergetic systems analysis side, and building the framework for the exergetic LCA on the life cycle assessment side.

Exergetic Systems Analysis
Given that two of our advanced carbon capture systems are adsorption-based (the MOF system and the biomimetic sorbent system), we chose to focus initially on building a general model for an adsorption system. When modeling such systems, many choices can be made about the nature of the system itself and of its cyclic operation. We have surveyed these choices and available modeling options, so that a decision could be made about the modeling direction to be taken. Fixed-bed adsorption systems can operate as pressure-swing adsorption (PSA) systems [14-16], vacuum-swing adsorption (VSA) systems [17, 18], or temperature-swing adsorption (TSA) systems [19]. Some systems combine the effects of changing both parameters, in pressure-temperature-swing adsorption (PTSA) [20]. Inside the bed, the sorbent is generally arranged as a packed bed of pellets, but there has been some recent exploration of different internal geometries, including monoliths and laminates [21].

Each of these choices carries corresponding simplifying assumptions in the mathematical treatment of the conservation equations in the bed. For example, models of PSA systems in which external heat transfer is negligible (for example, in short, wide columns) generally disregard the effect of radial gradients in temperature and gas-phase composition. This assumption is not accurate for TSA systems, due to the fact that the temperature swings are generated by heat transfer to a cooling/warming fluid, and that heat transfer is a direct result of radial temperature gradients in the column. Similarly, momentum conservation in fixed bed adsorption systems is typically represented by the

Ergun equation, which represents the pressure gradient in packed beds for a range of Reynolds numbers. However, if a different internal geometry of the bed is chosen—such as a monolith, which is specifically designed to reduce pressure drops—the momentum conservation relation will be represented quite differently.

This discussion is intended to motivate our chosen approach: to model the system as generally as necessary, using custom code written in Matlab. The need for generality is driven by two realities. First, in order to make substantial improvements in the exergy efficiency of carbon capture systems, or even to gain full understanding of the exergetic limitations of these systems, we may need to consider separation processes that go beyond traditional packed-bed PSA systems (e.g., a PTSA system with a monolith internal geometry). Second, our model will eventually use experimental data supplied from other GCEP research groups currently developing novel materials for carbon capture. These groups may indicate that these new materials operate best under a PSA process, or a TSA process, or a combination thereof. It is to our (and their) advantage to keep the model general at least until that time.

We have started building this model in Matlab, simulating the thermodynamic and transport properties of gases using the Cantera toolbox [22]. Mason et al.'s representation for the equilibrium loading of CO_2 and N_2 on certain MOFs and zeolites is used as a placeholder until we are supplied with the corresponding data from the GCEP research groups [23]. Mason et al.'s data is used because their fits are based on experimental data over a wide range of temperatures, instead of the single isotherms usually reported in the literature. The numerical scheme that will be used for our model is the weighted essentially non-oscillatory (WENO) scheme, based on research showing that this scheme lends itself well to modeling adsorption systems [18].

Finally, we have spent some time investigating Aspen Adsorption (formerly Aspen AdSim), AspenTech®'s flowsheet simulation tool for modeling adsorption systems. This software provides a remarkable range of options for adsorption modeling, including discretized models in two dimensions (such that TSA is possible), choices about heat exchanger placement, and an assortment of gas and sorbent properties. The energy and species balances can be solved in a rigorous way, including heat transfer to the tank walls and temperature differences between the gas and solid phases. However, a packed bed is still assumed for momentum balances. Moreover, the fact that Aspen Adsorption has such a wealth of options available makes it easy to inadvertently choose incompatible methods in a simulation. For example, while there are several options for numerical schemes—WENO not among them—some result in smearing of the solution around breakthrough fronts (these methods would be better suited to cyclic operation than to breakthrough simulations). The property methods used for gases and sorbents must be treated very carefully as well.

After studying the abilities of Aspen Adsorption, we determined that we will build custom code, to avoid loss of generality and to ensure full understanding of our system model. Where appropriate, we will develop Aspen models at points in the analysis for comparison with our custom model.

Exergetic Life-Cycle Analysis

    Work on the exergetic life-cycle analysis of CCS systems has progressed out of the initial planning and conceptualization stage, and initial implementation has begun. Methodologies for performing both the life-cycle assessment itself as well as the conversion of results into exergetic terms have been largely determined, and collection of data relevant to both calculations is underway. Purpose built code has been written for the creation of both 'technology' and 'intervention' matrices from raw data files. These matrices represent the interactions of all technologies within the "technosphere" (all human technological processes) and interactions of these technologies with the environment. Initial code has been developed to perform matrix-based LCA calculations, and to convert the resulting interventions vector to its exergetic components.

    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 v2.1 (2009)* life cycle assessment database, commissioned by the Swiss Centre for Life Cycle Inventories. The selection was based largely on the accessible nature of the raw database files, from which we could construct individual matrices and perform life-cycle assessments without the utilization of a third-party LCA software package. The *Ecoinvent v2.1* dataset contains detailed information on almost 4,000 processes, products, and services covering transport, building materials and construction, agricultural products, chemicals, plastics, metals, electronics, waste treatment and energy (including oil, natural gas, coal, nuclear energy, hydroelectric power, solar thermal and PV, and wind power). Also included are data on over 1,500 "elementary flows" to and from the environment (e.g. "Carbon dioxide, fossil origin") which may result from a given process, product, or service. Preliminary LCA work is currently progressing with the 2.1 version of the database, however version 3.0 is expected to be released later this year, and will expand the list of included products and processes to almost 10,000. We will adopt this dataset when it is released.

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

$$\boldsymbol{g} = (\boldsymbol{B}\,\boldsymbol{A}^{-1})\boldsymbol{f}\,, \tag{1}$$

where $\boldsymbol{f}$ is a final demand vector containing 1000 kg of monoethanolamine (MEA), a chemical used in our chosen baseline CCS technology, and $\boldsymbol{g}$ is the resultant environmental inventory vector created during the production of 1000 kg of monoethanolamine. The technology matrix **A** is, in general, a sparse nonsingular matrix with a poor condition number k of order 10^{22}. However, applying a consistent rescaling algorithm of the form

$$a'_{ij} = r_i a_{ij} c_j\,, \tag{2}$$

where r_i and c_j represent factors by which row i and column j are scaled respectively, reduces the condition number, leading to a more accurate inversion of the technology

matrix and more accurate calculations. Preliminary inventory results for aqueous fluxes from the production of 1000 kg of MEA are shown in Figure 1.
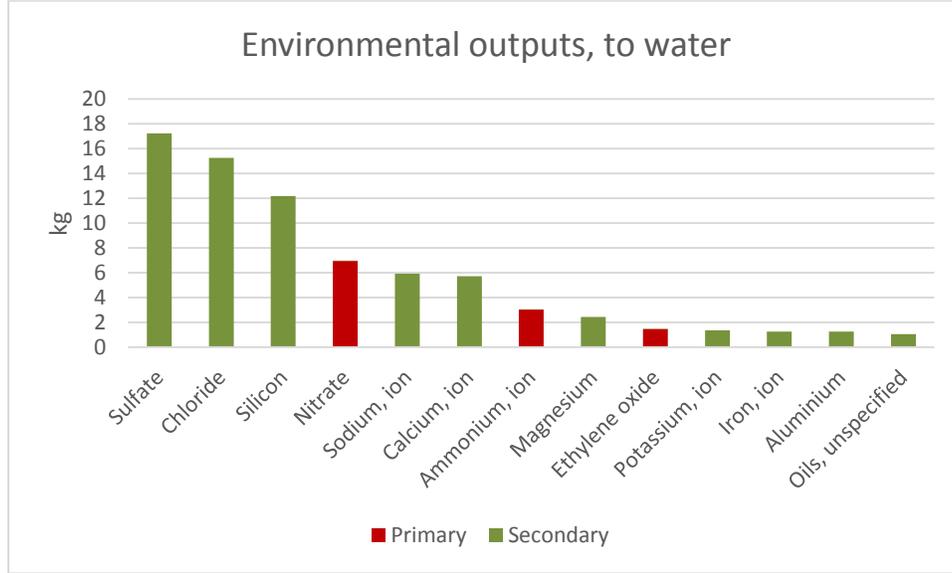

Figure 1: Primary and secondary emissions to water from the creation of 1000 kg of monoethanolamine, at chemical plant.

   In the interest of converting LCA inventory results like those outlined above into exergetic terms, a conceptual framework for performing the calculations has been developed and data necessary for the conversions (including heat capacity, environmental concentrations, and Gibbs free energy of formation for species of interest) is being collected. Chemical, thermal, and nuclear components of exergy have been accounted for, while the inclusion of land use change effects on biotic utilization of radiative exergy from the sun may be considered in the future. Chemical exergy calculations take the general form

$$B_{ch} = nT_0R \sum_i y_i \, ln\left(\frac{y_i}{y_{0i}}\right), \tag{3}$$

while the equation for the calculation of thermal exergy is

$$B_{th} = c_p\left(T - T_0 - T_0 ln\frac{T}{T_0}\right), \tag{4}$$

and nuclear exergy calculations are of the form:

$$B_{nuclear} = \frac{(\sum m_{i,p} - \sum m_{i,r})c^2}{\sum m_{i,r}}, \tag{5}$$

where y_i, y_{0i} equal the mole fraction of the ith component in a given substance and in the reference environment, c_p is the thermal capacity at constant pressure, c is the speed of

light in a vacuum, and m_i is the mass of the ith component before and after a nuclear reaction.

Progress

The project has progressed on two fronts. First, the development of a system model for a generalized adsorption unit for carbon capture is underway, using custom-written code in Matlab after surveying available commercial flowsheeting software. This will serve to analyze the systems-level performance, on an exergy basis, of new materials being developed for carbon capture by other GCEP research groups. Second, custom code has been written in Matlab to develop an exergetic life cycle assessment tool, with specific application to carbon capture systems. This will allow us to extend our analysis to a global scale, incorporating all exergetic transfers along the full life cycle of the carbon capture system.

Future Plans

This research project is still in early stages. Following the Gantt chart presented in our original GCEP proposal, future work will continue as outlined below. It is expected that some iteration over the process models will be necessary, as determined by the experimental data communicated to us from the other GCEP carbon capture groups.

- Develop the LCA exergetic framework (by summer 2013)
- Complete the adsorption process model (by autumn 2013)
- Complete the initial LCA of MEA reference system (by summer 2014)
- Build process model for the other systems (by autumn 2014)
- Develop the cost analysis framework (by autumn 2014)
- Complete the cost analysis of the MEA reference system (by winter 2015)
- Complete the cost analysis of the other systems (by autumn 2015)
- Complete the LCA modeling of the other systems (by autumn 2015)

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