HYDROPHOBIC PHYSICAL SOLVENTS FOR PRE-COMBUSTION CO₂ CAPTURE: EXPERIMENTS, COMPUTATIONAL SIMULATIONS, AND TECHNO-ECONOMIC ANALYSIS

Siefert, N.S.^{1,*}, Agarwal, S.,^{1,4} Shi, F.,³ Shi, W.,³ Roth, E.A.,^{1,4} Hopkinson, D.,¹ Kusuma, V.A.,^{1,4} Thompson, R.L.,³ Luebke, D.R.,¹ and Nulwala, H.B.^{1,2,*}

ABSTRACT

We synthesized and measured the properties of two new, hydrophobic, physical solvents to capture CO₂ from pre-combustion syngas streams at integrated gasification combined cycle (IGCC) power plants, and then estimated their levelized cost of capturing CO₂ (LCOC). The first solvent is an amphiphilic solvent containing polar ethylene glycol segments and non-polar siloxane portion (PEG-Siloxane-1). The second solvent is a hydrophobic ionic liquid: allyl-pyridinium bis(trifluoromethylsulfonyl)imide [aPy][Tf₂N]. The LCOC was estimated by importing physical properties of these solvents into AspenPlus, and then conducting a detailed, techno-economic analysis. Finally, the LCOC of these hydrophobic solvents was compared with the LCOC baseline solvent, Selexol. Our results suggest that PEG-Siloxane-1 is cost competitive with Selexol, and that [aPy][Tf₂N] could lower the cost of capturing CO₂ compared with Selexol, depending on the cost to synthesize this ionic liquid at commercial scale.

A. Introduction

In order to limit an increase in the average global temperature, sea level, and ocean acidity [1], future base-load coal power plants must capture CO₂ emissions. There has been increasing pressure for regulatory oversight on CO₂ emission from power plants, and most of these proposed regulations call for capturing the majority of CO₂ emission from new and existing power plants [2]. There are many coal power plant configurations that can capture enough carbon dioxide to meet these proposed regulations on greenhouse gas emissions, and there have been a number of studies that have estimated the levelized cost of electricity (LCOE) from such carbon capture and sequestration (CCS) power plants [3–11]. The LCOE takes into account the fixed maintenance costs, the variable operating costs, and the annualized costs on the upfront capital. The LCOE is an important figure of merit by which to compare power plants in similar markets with similar operating modes, such as base-load or peak-demand operation.

The studies referenced above have focused mainly on post-combustion CO₂ capture because of the large number of existing, base-load coal power plants across the globe that could be retrofitted with CCS technology. As for new power plants, integrated gasification combined cycle with carbon capture and storage (IGCC-CCS) is a promising technology to reach >90% CO₂ capture from fossil fuel power plants while also generating chemicals/fuels, such as hydrogen, ammonia or methanol [12,13]. At a gasification plant, carbon-containing fuels are gasified into a syngas containing fuel (H₂, CO, CH₄), inert species (CO₂, H₂O, N₂), and pollutants (H₂S, COS, Hg.) As found by Gerdes *et al.*¹, one major area for

improvement in the baseline IGCC-CCS process is the reduction of the energy penalty associated with cooling the syngas to below room-temperature in order to remove CO₂ and H₂S prior to combustion. As shown in Figures 4-1 and 4-3 of their report, Gerdes *et al.*¹ found that the electrical efficiency of an IGCC-CCS power plant could increase by 3 basis points, and the levelized cost of electricity could decrease by 20% when implementing warm gas clean-up of both pollutants and CO₂.

In most baseline IGCC-CCS reports, such as in the NETL bituminous baseline report by Black *et al.*², the acid gas removal solvent used is a hydrophilic solvent used in the commercially to remove acid gases and water from natural gas near room temperature before the gas enters a pipeline. While hydrophilicity is an ideal quality for a solvent in the natural gas industry, hydrophilicity is not ideal for IGCC-CCS applications. The ideal qualities of a physical solvent for IGCC-CCS applications are high CO₂ uptake, extremely high H₂S uptake, low uptake of H₂/CO/N₂/CH₄, high CO₂ diffusivity, low vapour pressure, low tendency to foam/aerosolize, high mass density, low water uptake, and most importantly operating stability above room temperature. Other important properties include: low cost starting materials, relatively simplistic synthesis, and environmentally-benign product. In order to surpass the baseline solvents, the overall levelized cost of capturing carbon dioxide using a novel solvent should be less than the overall levelized cost of using a baseline hydrophobic solvent.

Selexol, which is a proprietary solvent based on poly(ethylene glycol) dimethyl ether (PEGDME), has excellent H₂S and CO₂ uptake for a physical solvent, but it is also hydrophilic, which allows the solvent to absorb a significant amount of

water vapour from the treated stream [14]. Other solvents considered for pre-combustion CO₂ capture are volatile, water soluble compounds, such as methanol and acetone [15] as well as other low molecular weight hydrophilic polymers [16,17]. When using hydrophilic solvents for CO₂ capture, the syngas has to be cooled to or below room temperature in order to remove the water vapour from the fuel gas, which decreases net power and increases capital costs. To the author's knowledge, there have been no published economic analyses of an IGCC-CCS power plant in which the solvent is hydrophobic instead of hydrophilic, i.e. Selexol (UOP LLC, Des Plaines, IL) or Rectisol (Lurgi AG, Sasolburg, ZAF).

In this study, we report two novel hydrophobic solvents that have the potential to lower the levelized cost of capturing carbon dioxide in an IGCC power plant. The first solvent is a low molecular weight hybrid between PEGDME and a siloxane (Figure 1 Left). We will subsequently refer to this hybrid PEG-Siloxane solvent as PEG-Siloxane-1 solvent. The ‘-1’ label indicates that it was the first of many ways in which we have combined PEG and siloxane.

Siloxane-based solvents have a number of good qualities for CO₂ capture: (1) hydrophobic, (2) low vapour pressure and low viscosity, (3) low cost, and (4) high temperature stability. However, the CO₂/H₂ selectivity of pure siloxanes is poor compared with PEGDME [17]. By synthesizing a hybrid PEGDME-siloxane solvent (Figure 1 Left), we offset this undesirable property of siloxane while keeping the good qualities. Indeed compared with Selexol, this hybrid solvent has similar CO₂ solubility per litre of solvent, a lower viscosity, a higher molecular weight, and a much lower water uptake, making this solvent a very attractive alternative. In addition, the PEG-Siloxane-1 solvent is thermally stable up to 218°C, which gives a wider possible processing window for the gas separation.

Second, we have synthesized a new ionic liquid (allylpyridinium bis(trifluoromethylsulfonyl)imide, also abbreviated [aPy][Tf₂N] for convenience.) (Figure 1 Right) When compared against Selexol, [aPy][Tf₂N] has similar CO₂ solubility per litre of solvent, similar H₂ solubility, significantly lower vapour pressure, higher mass density, and significantly lower water uptake. These qualities are all preferable compared with Selexol, and make [aPy][Tf₂N] a very exciting physical solvent for warm gas CO₂ separation applications. Also, the viscosity of [aPy][Tf₂N] at 25°C (28 cP) is significantly lower than the viscosity of ionic liquids (100-10,000 cP) studied by previous researcher for CO₂ capture from pre-combustion syngas [18–20]. The excellent selectivity, the high-thermal stability, the extremely low vapour pressure, and the low viscosity are all reasons why we chose to analyze [aPy][Tf₂N] over the many other potential ionic liquids [21]. While the viscosity of [aPy][Tf₂N] at 25°C is four times higher than the viscosity of Selexol at 25°C (6 cP), this viscosity decreases rapidly with temperature, making it an interesting solvent for CO₂ capture between 40°C and 100°C.

Figure 1: Molecular structures of solvents used in this study PEG-PDMS-1 (Left) and [aPy][Tf,N] (Right)

Additionally, we have performed molecular simulations to understand why PEG-Siloxane-1 and [aPy][Tf₂N] have large CO₂ solubility and low H₂ solubility. We also show how the partial molar volume, which can easily be obtained from molecular simulations, but is difficult to obtain from experiments, is integrated with the raw experimental data to obtain more accurate gas solubility data at high gas pressure and large gas solubility.

Given that the economic cost of capturing CO₂ depends on many different properties, a techno-economic analysis conducted in AspenPlus (Aspen Technology, Burlington, MA) that compare the levelized cost of capturing CO₂ of the following three physical solvents: Selexol, PEG-Siloxane-1, and [aPy][Tf₂N]. This was done by regressing experimental data into AspenPlus, and then estimating the upfront capital and the reoccurring operating costs of the equipment needed to capture CO₂ from an existing IGCC power plant.

B. Experimental and Computational Results

(1) Solvent physical properties

In Table 1 and Table 2, we summarize the properties of PEG-Siloxane-1 and [aPy][Tf₂N], at 25°C and 40°C, respectively. For comparison, we list the properties of Selexol at this same range of temperatures. It should be noted that the viscosity of Selexol increases slightly with the addition of water, and that the values in Table 1 and Table 2 for Selexol are for the neat solvent. Experimental methods for the results and a full list of results can be found in the Supplemental Information, including gas solubility at 100°C.

Table 1: Summary of neat solvent properties at 25°C, 1 bar. The properties of PEG-Siloxane-1 and [aPy][Tf₂N] are experimentally measured, whereas the properties of Selexol are from AspenPlus [13]

Solvent	Density	Specific heat	Viscosity	Surface Tension	Thermal Conductivity
	(g·cm ⁻³)	(J·g ⁻¹ ·K ⁻¹)	(cP)	(N·m ⁻¹)	(W·m ⁻¹ ·K ⁻¹)
PEG-Siloxane-1	0.935	1.77	5.3	0.022	0.12
[aPy][Tf ₂ N]	1.507	1.11	28	0.036	--
Selexol	1.030	2.06	5.8	0.032	0.19

Table 2: Summary of neat solvent properties at 40°C, 1 bar. The properties of PEG-Siloxane-1 and [aPy][Tf₂N] are experimentally measured, whereas the properties of Selexol are from AspenPlus [13]

Solvent	Density	Specific heat	Viscosity	Surface Tension
	(g·cm ⁻³)	(J·g ⁻¹ ·K ⁻¹)	(cP)	(N·m ⁻¹)
PEG-Siloxane-1	0.921	1.78	3.38	0.021
[aPy][Tf ₂ N]	1.492	1.12	17.7	0.034
Selexol	1.026	2.15	4	0.031

In addition, we have fit parameters through the experimental data in order to estimate the properties of the solvents in the temperature range of 10°C – 100°C. The equations are listed to the right, and the values for the fitting parameters are given in Table 3.

$$\begin{aligned}\rho \text{ (g} \cdot \text{cm}^{-3}\text{)} &= \rho_0 + \rho_1 \cdot T(^{\circ}\text{C}) \\ c \text{ (J} \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-1}\text{)} &= A + B \cdot T(^{\circ}\text{C}) + C \cdot [T(^{\circ}\text{C})]^2 \\ c \text{ (J} \cdot \text{g}^{-1} \cdot ^{\circ}\text{C}^{-1}\text{)} &= A + B \cdot T(^{\circ}\text{C}) + C \cdot [T(^{\circ}\text{C})]^2 \\ \mu \text{ (cP)} &= \mu_0 \cdot e^{\beta/T(K)} \\ \sigma \text{ (N} \cdot \text{m}^{-1}\text{)} &= \sigma_0 + \sigma_1 \cdot T(^{\circ}\text{C})\end{aligned}$$

Table 3: Regressed parameters for the physical properties

Property	Units	Parameter	PEGDME	PEG-Siloxane-1	[aPy][Tf ₂ N]
Density	[kg·m ⁻³]	ρ_0	1080	956	1533
	[kg·m ⁻³ ·°C ⁻¹]	ρ_1	-1.21	-0.87	-1.01
Heat capacity	[J·g ⁻¹ ·°C ⁻¹]	A	1.94	1.77	1.10
	[J·g ⁻¹ ·°C ⁻²]	B	0.00645	-0.000400	0.000200
	[J·g ⁻¹ ·°C ⁻³]	C	-1.78E-06	1.60E-05	8.00E-06
Viscosity	[mPa·s]	μ_0	3.23E-06	4.92E-06	2.25E-06
	[K]	β	2269	2046	2811
Surface tension	[N·m ⁻¹]	σ_0	0.0378	0.0237	0.0369
	[N·m ⁻¹ ·°C ⁻¹]	σ_1	-0.00009	-0.00007	-0.00006

(2) Gas Solubility

In Figure 2, we present the CO₂ pure gas solubility at 25°C and 40°C in the three solvents that we analysed in detail: PEGDME, PEG-Siloxane-1, and [aPy][Tf₂N]. From an engineering point of view, CO₂ solubility per liter of lean solvent is more relevant than CO₂ solubility per mole or kilogram of lean solvent because the operating and capital costs associated with a given solvent are functions of the total volume, not mass or moles, of solvent looping through the process. For example, the power consumed in the main solvent pump is proportional to the volumetric flow rate of the lean solvent times the pressure difference between the low pressure and high pressure flash. This means that the pump power is inversely proportional to the slope of the curve between ~2 MPa and ~0.2 MPa in Figure 2.

It should also be noted that the CO₂ solubility in Selexol is plotted for neat solvent. Water absorption into Selexol takes away free volume where CO₂ or H₂ can accumulate. When modelling Selexol with 3wt% water accumulation, the CO₂ solubility decreased by 6% and the H₂ solubility decreased by 50%. Therefore, the net effect of water uptake in Selexol is mixed because the decrease in H₂ solubility is desirable, but the decrease in CO₂ solubility is undesirable. For PEG-Siloxane-1 and [aPy][Tf₂N], the water accumulation is less than 1 wt%, which has a negligible effect on both CO₂ and H₂ solubility.

At 25°C, there is an good match between the experimentally

measured solubility of CO₂ in PEG-Siloxane-1 and the computationally simulated solubility of CO₂ in PEG-Siloxane-1. In the Supplemental Section, we also present experimental data of CO₂ solubility at 100°C. In Figure 2a, we can also see that the CO₂ solubility at 25°C per litre of PEG-Siloxane-1 is slightly greater than the solubility in Selexol, and somewhat greater than in [aPy][Tf₂N].

This is likely due to the larger free molar volume fraction for PEG-Siloxane-1 compared with the [aPy][Tf₂N]. Our molecular simulations show that the free molar volume fraction for the PEG-Siloxane-1 at 298 K is 9.8%, which is larger than the value of 7.2% for the ionic liquid [hmim][Tf₂N] [22] and larger than the value of 5.2% for [aPy][Tf₂N]. This implies that for the same volume of solvents, the PEG-Siloxane-1 will have an 88% larger available free volume for CO₂ absorption than the [aPy][Tf₂N] ionic liquid. Due to the charged nature of ionic liquids, the cation-anion electrostatic interactions will bring these species close to each other, resulting in a more densely packing structure compared with non-ionic solvents. The highly packed structures in the ionic liquid leads to smaller available free volume per litre of ionic liquid for CO₂ absorption. As such, CO₂ exhibits a smaller solubility per liter solvent in ionic liquid than in PEG-Siloxane-1. Likewise, H₂ exhibits significantly larger gas solubility per liter solvent in PEG-Siloxane-1 than in [aPy][Tf₂N] or Selexol (Figure 3). Hence, there is a trade-off between high CO₂ solubility and high CO₂/H₂ selectivity in these two solvents.

Figure 2: CO₂ concentration (mol per litre of neat solvent) in physical solvents at 25°C (left) and 40°C (right.) The light, dashed line is the CO₂ solubility for Selexol as regressed into AspenPlus by Field and Brasington [13]. The black, filled squares are the experimentally measured values and the open, triangles are the computationally simulated values for PEG-Siloxane-1. The grey squares, open squares, and grey triangles are the experimentally measured values for [aPy][Tf₂N]. The black solid, the black dashed, and the grey solid lines are the solubility predicted by AspenPlus after all results from all temperature/pressures were regressed into AspenPlus, for PEG-Siloxane-1 Exp., PEG-Siloxane-1 Comp. Sim., and [aPy][Tf₂N], respectively.

Figure 3: H_2 concentration (mol per liter of neat solvent) in physical solvents at 25°C (left) and 40°C (right). The light, dashed line is the H_2 solubility for Selexol as regressed into AspenPlus by Field and Brasington [13]. The black, filled squares are the experimentally measured values and the open, triangles are the computational simulated values for PEG-Siloxane-1. The grey squares, open squares, and grey triangles are the experimentally measured values for [aPy][Tf₂N]. The black solid, the black dashed, and the grey solid lines are the solubility predicted by AspenPlus after all results from all temperature/pressures were regressed into AspenPlus, for PEG-Siloxane-1 Exp., PEG-Siloxane-1 Comp. Sim., and [aPy][Tf₂N], respectively.

C. System Analysis Methods

In order to conduct a techno-economic analysis of the solvents to determine which solvent might likely have the lowest levelized cost of capturing CO_2 , we modified an existing AspenPlus model of an IGCC-CCS power plant with two-stage removal of H_2S and CO_2 using Selexol [13]. The scale of this IGCC-CCS power plant is 1,155 MW of exergy in the syngas entering the absorber, 124 kg·s⁻¹ of CO_2 exiting the last stage of compression, and approximately 1,076 MW of exergy in the clean gas exiting the absorber. It should be noted that, from here on, we will be presenting our results on a normalized basis so that the results can be compared to analyses at different scales.

Figure 4: Process flow diagram for precombustion CO_2 capture using a physical solvent

While there are ways to use waste/low grade heat at an IGCC plant in order to decrease power consumption, we have decided to keep the CO_2 separation process the same as in Field and Brasington [13], which is shown in Figure 4 (Capture) and Figure 5 (Compression.) In future work, we plan include heat integration with other parts of the plant in order to operate the flash units at higher pressures and temperatures.

Figure 5: Process flow diagram for CO_2 -compression

The largest contributors to the cost of CO_2 capture in any IGCC-CCS power plant are: (a) Less electricity is being generated in the combined Brayton-Rankine cycle because H_2 (LHV = 240 kJ·mol⁻¹, Chemical Exergy = 236 kJ·mol⁻¹) is sent to the combustor rather than CO (LHV = 283 kJ·mol⁻¹, Chemical Exergy = 275 kJ·mol⁻¹) [23]. This decrease in power due to combusting H_2 rather than CO is approximately 15.4 kJ·mol⁻¹ of CO_2 captured;

and (b) electricity must be consumed to compress CO₂ from the partial pressure in the syngas (2 MPa) to the pressure of the CO₂ pipeline (15 MPa.) The compression costs are on the order of 10 kJ · mol⁻¹ of CO₂ captured. These two above mentioned sources of power loss make up roughly 76% of the power loss when adding CO₂ capture at an IGCC plant power, and they are independent of solvent used in the CO₂ capture process. In addition to these unavoidable costs, the solvent-unique operation costs are (a) the H₂ loss in the captured CO₂ that cannot be sent to the gas turbine, (b) the solvent pump power, (c) high the pressure (HP) flash recycle compressor power, (d) the low pressure (LP) CO₂ compressor power, and (e) the chiller unit power. We used AspenPlus to model both the electricity consumption and the capital costs of the equipment shown in Figure 4 and Figure 5.

(1) Absorber

The absorber has been modelled as an adiabatic Rate Based RADFRAC block in Aspen Plus without any reboiler. The feed-gas comes in from the bottom of the absorber and exits at the top. The temperature/pressure of the feed-gas is fixed at 40°C/5.2 MPa. The lean-solvent comes in from the top. The number of stages in the absorber and the flow rate of solvent are free variables, constrained by the requirement to capture 90% of the carbon in the syngas and the goal of minimizing the LCOC. The CO₂-rich solvent leaves the last stage of the absorber to go to the HP-FLASH block.

(2) Flash Blocks and Solvent Pump

The flash blocks are a three-stage regenerative process to recover CO₂-lean solvent. The HP flash block is used to recycle most of the captured H₂ back to the feed gas. All three flash units are modelled as equilibrium SEPARATOR blocks in Aspen Plus. These blocks are modelled as adiabatic processes. The pressures in these HP, MP, and LP flash units are free variables in the optimization routine to minimize LCOC. The solvent leaving the HP-Flash consequently goes to the MP and LP flash to release the absorbed gases. These LP-CO₂ and MP-CO₂ streams are sent to the CO₂ compression cycle for further processing, whereas the lean solvent after the LP-Flash is pumped back to the absorber (5.2 MPa.)

(3) Solvent Cooler/Chiller

In the two cases (Selexol and PEG-Siloxane-1) where the solvent is cooled to 10°C, a chiller is used to cool the solvent using 5°C chilled water. Butane is used as the refrigerant in the chiller system. It should be noted that a chiller unit was not used for [aPy][Tf₂N] because the LCOC was optimized at a temperature above room temperature. The range of allowed

temperatures for the solvent entering the absorber was 10-40°C. In future work, we plan to increase this temperature and increase the temperature of the feed gas entering the absorber in order to optimize this process.

D. Economic Analysis

This techno-economic analysis assumes that the CO₂ capture process is added to an existing IGCC plant with mercury, sulfur and other contaminant removal systems already in place. The new systems added are: Water Gas Shift (WGS) reactors, a physical solvent-based capture system, and a CO₂ compression system. To the bare equipment capital costs (BEC) calculated by AspenPlus, we apply a plant cost ratio (PCR) of 5 to obtain the Total Capital Cost for the system from the raw equipment capital cost. Also called a Lang Factor, a PCR was used to incorporate engineering and contingency costs for retrofitting systems [24]. In Figure 6, we show a breakdown of the capital cost of the major pieces of equipment when using PEG-Siloxane as the solvent. The breakdown is similar for Selexol and [aPy][Tf₂N], though with slightly different absolute values of capital cost. For PEG-Siloxane-1, 43% of the capital cost is due to the CO₂ compressors; 28% is due to the absorber; 11% is due to the chiller; 9% is due to the WGS reactor; 5% is due to the recycle compressor and cooler for the gas leaving the HP flash unit; 3% is due to all three flash units; and only 1% of the capital cost is due to the solvent pump.

Figure 6: Capital Cost Distribution Chart for CO₂ Capture and Compression System using PEG-Siloxane-1.

In Figure 7, we show a breakdown of the operating costs of the major pieces of equipment when using PEG-Siloxane-1 as the solvent. The largest operating cost is the loss in power output due to combusting H_2 rather than CO , which is approximately $15.4 \text{ kJ} \cdot \text{mol}^{-1}$ of CO_2 captured when accounting for power loss in both the Brayton and Rankine cycles. The second largest operating cost is the electricity consumption in the MP and HP CO_2 compressors from 1.1 MPa to 15 MPa (22%.) Smaller amounts of electricity are consumed in the solvent pump (7%), the LP compressor (6%), the chiller (6%), and the recycle compressor/cooler (3%). Finally, 2% of the total operating cost is due to the loss of H_2 in the compressed CO_2 stream that would have gone to the gas turbine cycle and generated electricity.

Figure 7: Operating Electricity Loss/Consumption Distribution Chart for CO_2 Capture and Compression System using PEG-Siloxane-1

The upfront capital and the annual operating costs were then used to calculate the levelized cost of capturing carbon dioxide (LCOC). Here, we define the LCOC to be equal to the price that one would have to sell the compressed CO_2 such that the net present value (NPV) of the capture/compression equipment is equal to zero. The equation for the NPV of a cash flow time series between year $t=0$ and year $t=N$ is given in equation form below:

$$NPV = \sum_{t=0}^{t=N} [(CO_2 \text{ Revenue})_t - (Cost)_t] \cdot (1+i)^{-t}$$

By setting the NPV equal to zero, we can solve for the required CO_2 revenue, which is equal to the LCOC times the amount of CO_2 captured. In equation form, the LCOC is the

net present cost of all expenses due to CO_2 capture divided by the net present amount of all CO_2 captured:

$$\text{Levelized Cost of } CO_2 \text{ Captured} \left[\frac{\$}{\text{tonne } CO_2} \right] = \frac{\sum_{t=0}^{t=N} (Cost)_t \cdot (1+i)^{-t}}{\sum_{t=0}^{t=N} (CO_2 \text{ Captured})_t \cdot (1+i)^{-t}}$$

where $(Cost)_t$ is the costs accrued in year t in FY2012 dollars, $(CO_2 \text{ Captured})_t$ is the metric tonnes of CO_2 captured in year t , N is the lifetime of the plant, and i is the annual discount rate. This equation can be broken down into a summation of operating costs and capital costs by assuming a price for electricity that is lost due to the lower electricity generation at the IGCC-CCS plant compared with the IGCC plant. The equation for the LCOC becomes the following:

$$\begin{aligned} \text{Levelized Cost of } CO_2 \text{ Captured} \left[\frac{\$}{\text{tonne } CO_2} \right] &= \frac{\text{Power Decrease [MW]} \cdot \text{Electricity Cost} \left[\frac{\$}{\text{MWh}} \right]}{CO_2 \text{ Captured} \left[\frac{\text{ton}_{CO_2}}{\text{hr}} \right]} \\ &+ \frac{PCR \cdot BEC [\$] \cdot \frac{1}{365 \cdot 24} \left[\frac{\text{yr}}{\text{hr}} \right]}{\text{Capacity Factor [-]} \cdot CO_2 \text{ Captured} \left[\frac{\text{ton}_{CO_2}}{\text{hr}} \right]} \\ &\cdot \left(\frac{i(1+i)^N}{(1+i)^N - 1} + O\&M \right) \left[\frac{1}{\text{yr}} \right] \end{aligned}$$

where PCR is the plant cost ratio, BEC is the bare equipment costs, capacity factor is the fraction of the time that the power plant is operating at its design operating power, and O&M is the yearly operating and maintenance costs as a fraction of original total capital costs. The assumptions used in this economic analysis are summarized in Table 4. It should be noted that these assumptions had no effect on the relative LCOC of Selexol versus PEG-Siloxane-1.

To avoid confusion between the many different ways that researchers estimate the cost of capturing CO_2 or the cost of CO_2 avoided, we present our estimated cost of CO_2 captured in PEG-Siloxane-1 and [aPy][Tf₂N] normalized by our estimated cost to capture CO_2 using Selexol. In Figure 8, we present a summary of the results from the economic model. The values for the data shown in Figure 8 can be found in Table S3 in the Supplemental Information.

As seen in Figure 8, the majority of the levelized cost of capturing CO_2 from an IGCC power plant is independent of the solvent used. As mentioned earlier, there are unavoidable costs associated with (a) combusting H_2 rather than CO , (b) MP/HP CO_2 compression capital costs, and (c) MP/HP CO_2

compression operating costs. This is part of the reason why the PEG-Siloxane-1 solvent obtained essentially the same levelized cost of capturing CO₂ (100%) as Selexol. One important note regarding Selexol is that the cost of the solvent (~\$4·L⁻¹) is such that the cost to initially purchase the material and to continually make-up solvent is negligible compared with the other capital and operating costs. We have assumed a value of \$4·L⁻¹ for the cost of the PEG-Siloxane-1 solvent because the starting materials (PEG and siloxane) are both relatively low cost.

Table 4: Assumptions in Economic Analysis

Variable	Assumed Value	Unit
Electricity Cost	\$50	[MWh ⁻¹]
Plant Cost Ratio	5	[-]
Capacity Factor	80%	[-]
Construction Time	1	[yr]
Lifetime, N	30	[yr]
O&M	4% of upfront capital per year	[yr ⁻¹]
CO ₂ Capture	90% of C in coal	[-]
Inflation rate	0%	[yr ⁻¹]
Discount rate, i	7%	[yr ⁻¹]

The most significant unknown in our techno-economic analysis is the price of [aPy][Tf₂N] at commercial scale. Currently, the price of the [Li][Tf₂N] used as a starting material to synthesize the [aPy][Tf₂N] solvent represents a major cost, and current prices to produce ~100 g scale of material costs on the order of \$2000·L⁻¹. We expect that this cost will decrease significantly with large scale production of [Tf₂N]-based ionic liquids. In Figure 8, we have assumed a best-case value of \$40·L⁻¹ for the cost to synthesize the [aPy][Tf₂N] ionic liquid. Using this value, we estimate that the [aPy][Tf₂N] ionic liquid has the potential to lower the LCOC by 7% compared to Selexol. The lower costs come from both lower capital and operating costs for the capture equipment, since the [aPy][Tf₂N] can be operated at higher temperatures without absorbing significant amount of water

vapour and without evaporating, and also because the [aPy][Tf₂N] has a higher mass density than Selexol, which decreases the size/cost of the absorber and flash units because gas/liquid separation can occur at higher values of gas velocity. In addition, the negligible vapour pressure of [aPy][Tf₂N] reduces the amount of solvent required to make up lost solvents due to evaporation. However, if instead the cost to synthesize [aPy][Tf₂N] is a worst-case value of \$400·L⁻¹, then the cost to capture CO₂ using [aPy][Tf₂N] could be 16% greater than Selexol or PEG-Siloxane. The black box in Figure 8 represents the range in LCOC values if the cost of the solvent is between \$40·L⁻¹ and \$400·L⁻¹. A value of \$40·L⁻¹ is already included in the levelized capture capital and operating cost, so the black area represents costs on top on \$40·L⁻¹. As such, it will be crucial to keep the mass-production- costs of [aPy][Tf₂N] to less than \$125·L⁻¹ in order for this ionic liquid to outperform Selexol or PEG-Siloxane-1.

Figure 8: Comparison of Levelized Cost of Capture

E. Conclusions

We have measured the properties of two hydrophobic, physical solvents that can be used to capture CO₂ from pre-combustion syngas streams at an IGCC-CCS power plant or at a gasification based chemical synthesis plant. In addition, we have computationally simulated the properties of the PEG-Siloxane-1 solvent. We estimate the cost of capturing CO₂

using these solvents by performing a regression of the physical properties of these solvents into AspenPlus, followed by a techno-economic analysis. We found that most of the unavoidable costs of capture are independent of the solvent being used. Therefore, using a hydrophobic, lower density, high CO₂ uptake solvent such as the PEG-Siloxane-1 solvent in the conventional Selexol process has relatively minimal impact on the cost of capture. We found that more significant decreases in cost of capture can potentially be achieved with a hydrophobic ionic liquid solvent, such as [aPy][Tf₂N], mostly due to the higher operating temperature and the higher mass density. The higher operating temperature enabled by the low volatility ionic liquids reduces the energy penalty from cooling the syngas stream for separation. The high density leads to reduction in the size and cost of the absorber and flash units because gas/liquid separation can occur at higher values of gas velocity. In order to realize the potential advantages of this ionic liquid on pre-combustion CO₂ capture, however, the materials cost must be reduced to below \$125·L⁻¹ for it to be a viable alternative to Selexol.

In future work, we plan to modify the pressure-swing-only process flow diagram used in this paper by allowing both temperature and pressure swing. This will take advantage of the larger operating temperature window for PEG-Siloxane-1 and [aPy][Tf₂N], and to possibly decrease the LCOC by using waste heat or low grade heat at the IGCC power plant to raise the temperature and pressure of the flash units.

F. Acknowledgements

We thank Lynn Brickett, Brian Chang, Jeff Culp, Robert Enick, Alex Hallenbeck, Brian Kail, John Kitchin, Peter Koronaios, Michael Matuszewski, Megan Macala, David Miller, Sarah Narburgh, Regina Woloshun, Paul Zandhuis, Matthew Zeh, and Xu Zhou. This technical effort was performed in support of the U.S. Department of Energy's National Energy Technology Laboratory's fiscal year 2015 Carbon Capture field work proposal. This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe on privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency

thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Notes and references

¹ Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA, USA

² Carnegie Mellon University, Chemistry Department, Pittsburgh, PA, USA

³ AECOM/URS Corporation, National Energy Technology Laboratory, Pittsburgh, PA, USA

⁴ Fellow, Oak Ridge Institute for Science and Education

*Corresponding authors: nicholas.siefert@netl.doe.gov, hnulwala@andrew.cmu.edu

- [1] IPCC 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press; 2013.
- [2] Stauffer PH, Keating GN, Middleton RS, Viswanathan HS, Berchtold KA, Singh RP, et al. Greening coal: breakthroughs and challenges in carbon capture and storage. *Environ Sci Technol* 2011;45:8597–604. doi:10.1021/es200510f.
- [3] Herzog HJ. The Economics of CO₂ Capture. In: Reimer P, Eliasson B, Wokaum A, editors. *Greenh. Gas Control Technol.*, Oxford: Elsevier; 1999, p. 101–6.
- [4] Johnson TL, Keith DW. Fossil electricity and CO₂ sequestration: how natural gas prices, initial conditions and retrofits determine the cost of controlling CO₂ emissions. *Energy Policy* 2004;32:367–82. doi:10.1016/S0301-4215(02)00298-7.
- [5] Rubin ES, Chen C, Rao AB. Cost and performance of fossil fuel power plants with CO₂ capture and storage. *Energy Policy* 2007;35:4444–54. doi:10.1016/j.enpol.2007.03.009.
- [6] Rubin ES, Mantripragada H, Marks A, Versteeg P, Kitchin J. The outlook for improved carbon capture technology. *Prog Energy Combust Sci* 2012;38:630–71. doi:10.1016/j.pecs.2012.03.003.
- [7] Davison J. Performance and costs of power plants with capture and storage of CO₂. *Energy* 2007;32:1163–76. doi:10.1016/j.energy.2006.07.039.
- [8] Kunze C, Spliethoff H. Modelling of an IGCC plant with carbon capture for 2020. *Fuel Process Technol* 2010;91:934–41. doi:10.1016/j.fuproc.2010.02.017.

- [9] Hammond GP, Akwe SSO, Williams S. Techno-economic appraisal of fossil-fuelled power generation systems with carbon dioxide capture and storage. *Energy* 2011;36:975–84. doi:10.1016/j.energy.2010.12.012.
- [10] Connell DP, Lewandowski D a., Ramkumar S, Phalak N, Statnick RM, Fan L-S. Process simulation and economic analysis of the Calcium Looping Process (CLP) for hydrogen and electricity production from coal and natural gas. *Fuel* 2013;105:383–96. doi:10.1016/j.fuel.2012.07.006.
- [11] Li M, Rao AD, Scott Samuelsen G. Performance and costs of advanced sustainable central power plants with CCS and H₂ co-production. *Appl Energy* 2012;91:43–50. doi:10.1016/j.apenergy.2011.09.009.
- [12] Figueroa JD, Fout T, Plasynski S, McIlvried H, Srivastava RD. Advances in CO₂ capture technology—The U.S. Department of Energy’s Carbon Sequestration Program. *Int J Greenh Gas Control* 2008;2:9–20. doi:http://dx.doi.org/10.1016/S1750-5836(07)00094-1.
- [13] Field RP, Brasington R. Baseline Flowsheet Model for IGCC with Carbon Capture. *Ind Eng Chem Res* 2011;50:11306–12. doi:10.1021/ie200288u.
- [14] Yave W, Car A, Peinemann K-V. Nanostructured membrane material designed for carbon dioxide separation. *J Memb Sci* 2010;350:124–9. doi:10.1016/j.memsci.2009.12.019.
- [15] Miller MB, Chen D-L, Xie H-B, Luebke DR, Karl Johnson J, Enick RM. Solubility of CO₂ in CO₂-philic oligomers; COSMOtherm predictions and experimental results. *Fluid Phase Equilib* 2009;287:26–32. doi:10.1016/j.fluid.2009.08.022.
- [16] Miller MB, Luebke DR, Enick RM. CO₂-philic Oligomers as Novel Solvents for CO₂ Absorption. *Energy & Fuels* 2010;24:6214–9. doi:10.1021/ef101123e.
- [17] Enick RM, Koronaio P, Stevenson C, Warman S, Morsi B, Nulwala H, et al. Hydrophobic Polymeric Solvents for the Selective Absorption of CO₂ from Warm Gas Streams that also Contain H₂ and H₂O. *Energy & Fuels* 2013;27:6913–20. doi:10.1021/ef401740w.
- [18] Thompson RL, Shi W, Albenze E, Kusuma VA, Hopkinson D, Damodaran K, et al. Probing the effect of electron donation on CO₂ absorbing 1,2,3-triazolide ionic liquids. *RSC Adv* 2014;4:12748. doi:10.1039/c3ra47097k.
- [19] Götz M, Orloff F, Reimert R, Basha O, Morsi BI, Kolb T. Evaluation of Organic and Ionic Liquids for Three-Phase Methanation and Biogas Purification Processes. *Energy & Fuels* 2013;27:4705–16. doi:10.1021/ef400334p.
- [20] Basha OM, Heintz YJ, Keller MJ, Luebke DR, Resnik KP, Morsi BI. Development of a Conceptual Process for Selective Capture of CO₂ from Fuel Gas Streams Using Two TEGO Ionic Liquids as Physical Solvents. *Ind Eng Chem Res* 2014;53:3184–95. doi:10.1021/ie403375m.
- [21] Brennecke JF, Gurkan BE. Ionic Liquids for CO₂ Capture and Emission Reduction. *J Phys Chem Lett* 2010;1:3459–64. doi:10.1021/jz1014828.
- [22] Shi W, Sorescu DC, Luebke DR, Keller MJ, Wickramanayake S. Molecular Simulations and Experimental Studies of Solubility and Diffusivity for Pure and Mixed Gases of H₂, CO₂, and Ar Absorbed in the Ionic Liquid 1-n-Hexyl-3-methylimidazolium Bis(Trifluoromethylsulfonyl)amide ([hmim][Tf₂N]). *J Phys Chem B* 2010;114:6531–41. doi:10.1021/jp101897b.
- [23] Moran MJ, Howard N Shapiro. *Fundamentals Of Engineering Thermodynamics*. 2004. doi:10.1177/004057368303900411.
- [24] Seider WD, Seader JD, Lewin DR. *Process Design Principles: Synthesis, Analysis, and Evaluation*. Wiley; 1999.

National Energy Technology Laboratory Internal Report References

1. K. Gerdes *et al.*, Current and Future Technologies for GasificationBased Power Generation, DOE/NETL-2009/1389, 2010.
2. J. Black *et al.*, Cost and Performance Baseline for Fossil Energy Plants: Volume 1 Rev 2a, DOE/NETL-2010/1397, 2013.

Pre-combustion CO₂ Capture

PEGDME
Selexol™
hydrophilic
0-30°C

PDMS-PEGDME
H-Siloxane
hydrophobic
10-40°C

[aPy][Tf₂N]
Ionic Liquid
hydrophobic
40-100°C