Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information for

A Single-Component Water-Lean Post-Combustion CO_2 Capture Solvent with Exceptionally Low Operational Heat and Total Costs of Capture – Comprehensive Experimental and Theoretical Evaluation

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Section S1: Solvent Synthesis

Procedure and spectral details:

Briefly, the synthesis of N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA) follows a 1 step reaction (neat) of 3-aminopropylmorpholine (2.9 equivalent) and bromoethyl ethyl ether (1 equivalent) at 80 °C to afford 2-EEMPA in 86% yield after fractional vacuum distillation. To a 500 mL three-necked round-bottom flask equipped with a magnetic stir bar, addition funnel, an alcohol thermometer, and ground glass stopper was added 310 mL (307 g, 2.13 mol) 3-aminopropylmorpholine under nitrogen atmosphere. The amine was heated to an internal temperature of 80 °C and then 95.0 mL (116 g, 0.739 mol) of technical grade (90%) 2-bromoethyl ethyl ether was added dropwise to the neat amine. The internal temperature rose to approximately 110 °C and held steady until the complete addition. The reaction was allowed to slowly cool back to 80 °C and stirred overnight. The addition funnel was swapped with a short path distillation head, and the excess amine was distilled under reduced pressure. The 'gum-like' residue was poured warm into 250 mL chloroform chilled on ice and washed with (2 x 250 mL) 10 M KOH (aq.) and (1 x 250 mL) distilled water. The organic layer was separated, and the combined aqueous washes were back extracted with 200 mL chloroform. The combined organic layer was dried over Na_2SO_4, filtered and evaporated. The product was distilled under reduced pressure (150 microns), the distillation apparatus equipped with a 17.5 cm Vigreux column and a short path equipped with a short Vigreux connection. Fractions at 100–105 °C contained 2-EEMPA and were combined yielding an approximate 138 g (86.3% yield). This synthesis was repeated until an adequate amount of solvent had been collected for further testing.

Attenuated total reflectance infrared spectroscopy (ATR-IR) measurements were performed on a diamond crystal (angle of incidence, 45.0°; number of bounces, 1.0; sample refractive index, 1.50) using a Nicolet Magna-750 spectrometer running OMNIC software. The spectra (**Figure S1**) were recorded over 700−4000 cm^{-1} with a resolution of 4 cm^{-1}.

^1H and ^{13}C NMR (**Figures S2** and **S3**) were also collected on 2-EEMPA in $CDCl_3$ to confirm product formation as originally described by Cantu et al.[1] MS calculated $[M+H^+]$ for $C_{11}H_{25}N_2O_2^+$ is 217.19 and found 217.19.

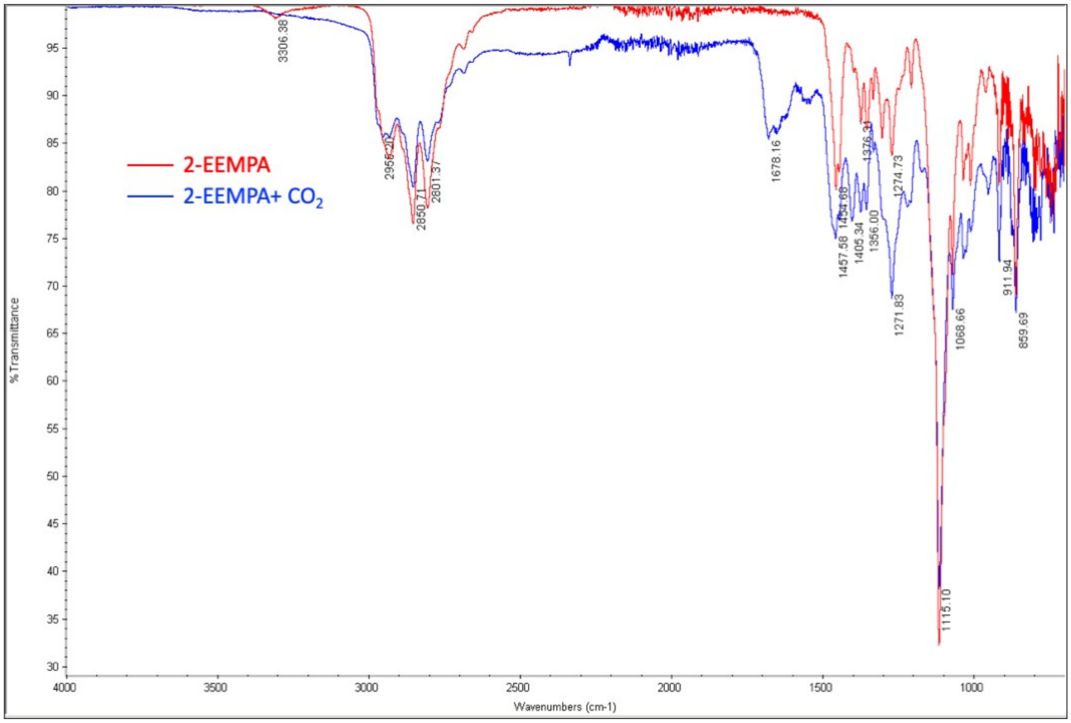

Figure S1: ATR-IR for 2-EEMPA and CO_2 bound 2-EEMPA

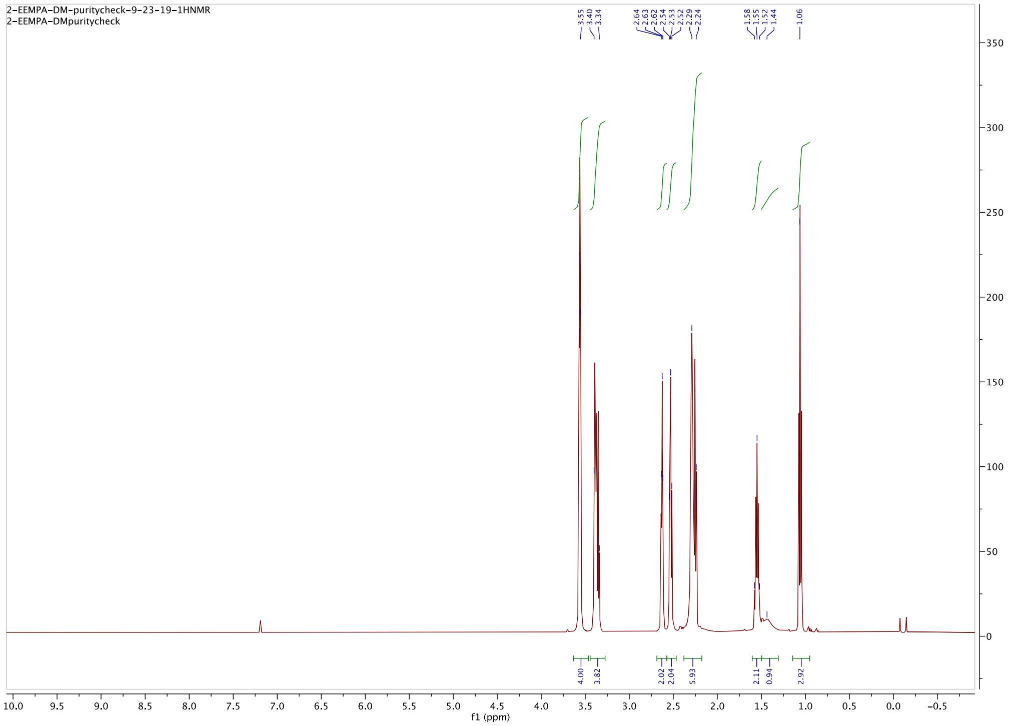

Figure S2: ^{1}H NMR on 2-EEMPA. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.06 (3H, t, *J* = 5.0 Hz), 1.44 (1H, bs), 1.55 (2H, p, *J* = 5.0 Hz), 2.24-2.29 (6H, m), 2.53 (2H, t, *J* = 5.0 Hz), 2.63 (2H, t, *J* = 5.0 Hz), 3.32-3.40 (4H, m), 3.55 (4H, t, *J* = 5.0 Hz).

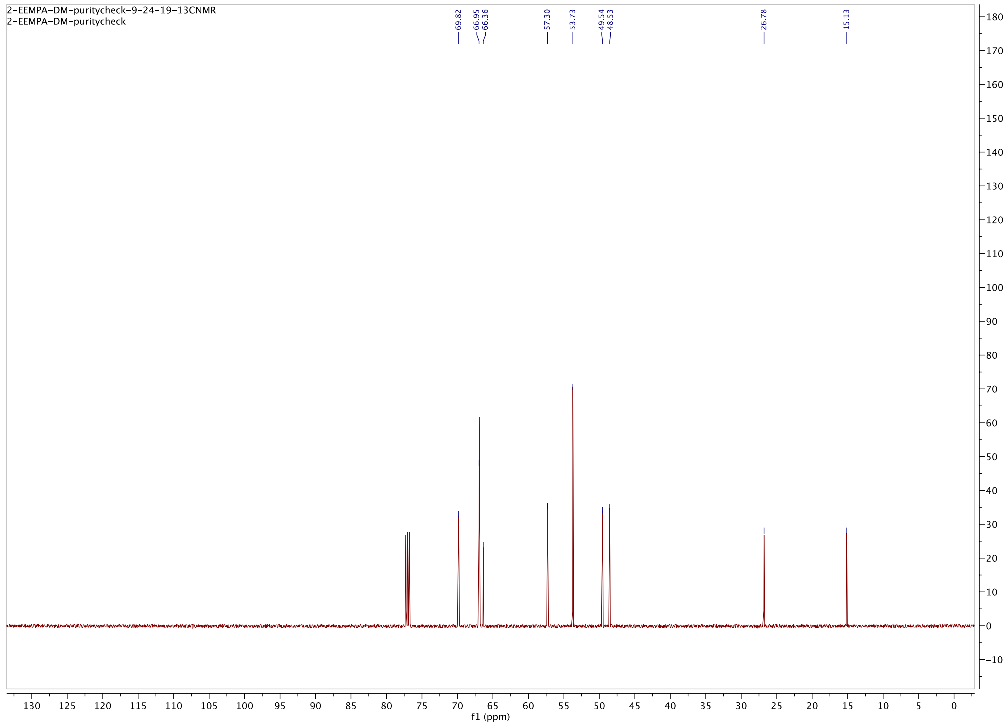

Figure S3: 13C NMR on 2-EEMPA. ($CDCl_3$, 125.7 MHz): 69.8, 66.9, 66.4, 57.3, 53.7, 49.5, 48.5, 26.8, 15.1 ppm.

Section S2: Solvent Characterization

PVT experiment

Both equilibrium and kinetic measurements are performed on our custom PTx cell instrument designated as the PVT apparatus. Although a more thorough analysis of the design and analysis of this custom equipment has been explored in our other work, a summary of the experimental methodology is provided herein.

As with traditional PTx cells, the volume of the cell is known and calibrated such that the gas pressure can be used to derive molar concentrations. In our design the solvent is in constant recirculation in and out of the cell such that the solvent is well mixed and the concentration of gas in the solvent is homogenous. With a designed contactor surface, the area of gas-liquid interface is known, fixed and calibrated. In the experiment, a known volume pure CO_2 at sub-atmospheric pressures is injected into the PTx cell and allowed to equilibrate with the recirculating solvent. During this process, in situ raw data of gas phase pressure and temperature is collected as a function of time. Data regression of this raw data takes advantage of the known fixed calibrated volumes of the cell and the gas manifold to determine molar concentrations of the assumed ideal gas at any given time. The ratio of molar concentration of CO2 in the solvent to the molar concentration of solvent in the system represents the liquid loading of CO_2, α, that is used as an independent variable across both equilibrium and kinetic measurements.

Multiple injections of known volumes of CO2 in small doses are introduced into the cell and absorption occurs. When the cell pressure stabilizes, the solvent is assumed to be in equilibrium and the corresponding loading of CO2 can determined. This represents one point on the isotherm for VLE and injections continue as cell pressure increases and equilibrates in this cycle. In this way, VLE data can be regressed and the same experiment can be conducted with varying cell temperatures to understand the temperature dependency.

For kinetics analysis, time dependent cell pressure data is further regressed. Since pure gas is used, the gas film mass transfer resistance is negligible and it is assumed that the mass transfer of CO_2 into the solvent is only limited by liquid film resistance. Thus, this resistance can be expressed by the mass transfer coefficient using a mathematical expression for molar flux and derived directly from experimental data (Eq. S1)

$$k_g^{'} = \frac{RT}{V_{cell} \cdot A}\left(\frac{\partial \ln\left(P - P^*\right)}{\partial t}\right)_{T,V} \qquad \textbf{(Eq. S1)}$$

WWC experiment

The reference instrument for VLE measurements is a wetted-wall contactor column apparatus routinely used for solvent sorption characterization in literature. A detailed description of this apparatus and the subsequent data regression is provided in our previous contributions, 1) Mathias et al. ChemSusChem, 2015, 8, 3617-3625 and 2)Whyatt et al. Ind. Eng. Chem. Res. 201, 56, 16, 4830-4836.

VLE Comparison of 2-EEMPA with MEA

The VLE data for 2-EEMPA was compared with MEA using the correlation for liquid film mass transfer coefficient, kg’, as a function of CO_2 equilibrium pressure, P*. This comparison is shown in **Figure S4** below. This comparison relies on the following assumptions: 1) the same feed gas CO_2 concentration is used, 2) the same product flue gas concentration is achieved, 3) an allowable delta P (gas partial pressure to equilibrium partial pressure) is used, 4) a similar solvent mass with similar regeneration energy is utilized (without detailed TEA analysis). These assumptions allow for this “quick” comparison of kinetic performance between these two solvents. A more thorough comparison will incorporate overall process economics in a future contribution.

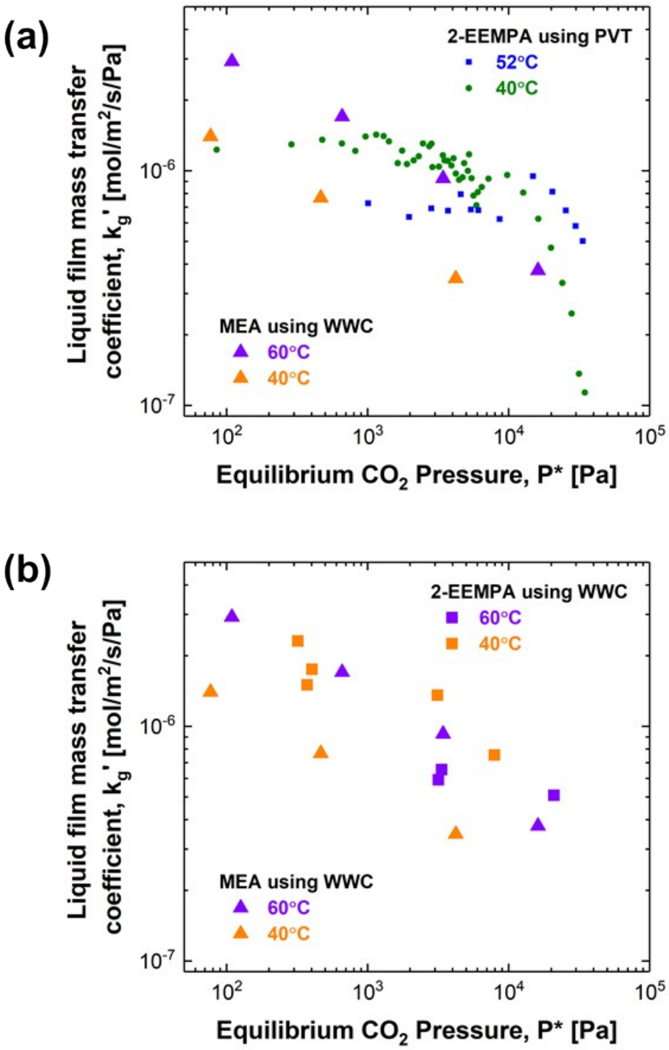

Figure S4. Comparison of VLE data between 2-EEMPA and MEA at similar temperatures with data collected for 2-EEMPA in a) PVT apparatus and b) WWC apparatus.

Section S3: LCFS

System shakedown

Prior to testing with flue gas simulant, a routine gas comprised solely of nitrogen, carbon dioxide and water was utilized for shakedown of the apparatus (Table 1). The purpose of shakedown was to identify an optimal set of conditions for operation with the flue gas simulant. To do so, a series of parametric tests was performed using our four control variables. A 12-run Latin hypercube design was chosen to populate the 4-factor test matrix within a set of limits to the process conditions (Table S1). Thus, each variable dimension is divided by 12 evenly placed grid points and then a set of sample points are picked randomly with the constraint that any hyperplane will contain just one sample point. The resulting matrix of test conditions for this parametric shakedown test are also shown in Table S1.

	Solvent Flow Rate [L/min]	**Gas Flow Rate [slm]**	**Reboiler Temperature [°C]**	**Absorber Temperature [°C]**
Range	0.15 – 0.50	10 – 65	100 – 120	30 – 50
Run	**L**	**G**	$T_{Reboiler}$	$T_{Absorber}$
1	0.405	35	120.0	35.5
2	0.341	25	118.2	48.2
3	0.309	65	116.4	44.5
4	0.150	40	110.9	46.4
5	0.468	60	114.5	37.3
6	0.436	45	103.6	50.0
7	0.182	15	112.7	33.6
8	0.245	50	100.0	39.1
9	0.214	55	107.3	31.8
10	0.373	30	105.5	30.0
11	0.277	10	101.8	42.7
12	0.500	20	109.1	40.9

Table S1. Matrix of conditions for parametric series of shakedown tests performed on LCFS.

For each run case performed on the LCFS, a corresponding capture efficiency was recorded as defined by the ratio of CO_2 captured by the solvent to the amount of CO_2 entering in the inlet gas. Results from the parametric series of tests show that the capture efficiency was the most sensitive to the feed gas flow rate in this LCFS configuration (Figure S5). Based on this data, the test conditions chosen for operation of LCFS to target a >90% capture efficiency with flue gas simulant were as follows: dry gas flow rate of 12.5 slm, 0.24 L/min for solvent circulation, 40°C absorber column temperature, and 115°C reboiler temperature.

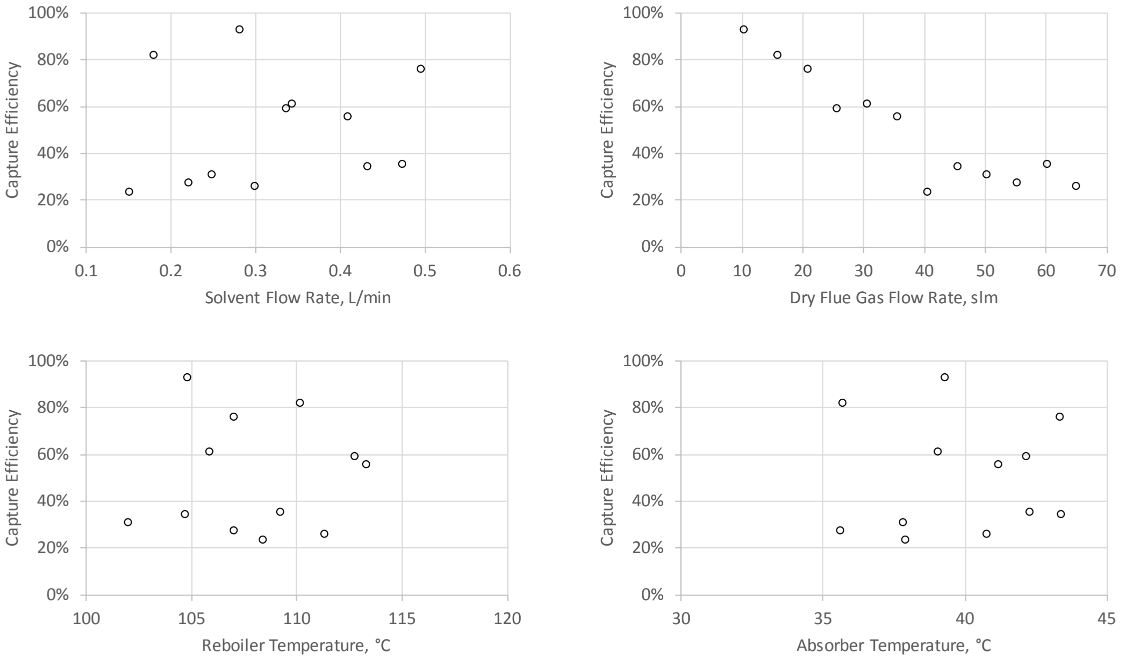

Figure S5. Results of parametric shakedown tests for LCFS.

Liquid Sampling

Prior to operation, solvent was loaded into the column via a stand-alone gear pump plumbed from a stock bottle directly into the top of the absorber. Each column has a 1 L collection reservoir tank directly below it. As the solvent filled the absorber reservoir, the absorber pump was run to push solvent to the stripper circuit to keep the levels near even. When full, both absorber and stripper pumps were run to achieve cross flow.

Liquid samples were collected at various points during solvent testing. A sample set consisted of two 2mL liquid samples, stored in 2mL screw cap GC vials to eliminate head space. A 3 mL syringe and needle were used in conjunction with a septum sampling port in-line to extract the samples from the process plumbing. One sample was collected from immediately after the rich solvent pump prior to entering the cross heat exchanger and the other in-line sample port was located directly upstream of lean solvent entry into absorber, after the cross heat exchanger.

H_2O and CO_2 Loading Analysis on EEMPA

Solvent samples were collected from LCFS and processed for subsequent composition analysis. Water content was analyzed via Karl-Fischer titration using a Mettler Toledo C20 coulometric KF Titrator. The solvent samples were syringed, weighed, and injected into the instrument which automatically provided an estimate of water content (in ppm) based on input weight. Two additional repetitions were performed to obtain an average water content per sample.

A unique GC-MS method was specifically developed for EEMPA to quantify the CO_2 and also to verify H_2O content in samples. Sample analysis was accomplished using an Agilent Technologies (Santa Clara, CA) 7890 Gas Chromatograph coupled to an Agilent Technologies 5975C Inert XL MSD. Neat 1.0 ul EEMPA samples were injected by an Agilent 7693 Autosampler to the 275C injection port configured with a 100 to 1 gas split ratio with a constant column helium back pressure of 20psi. Due to sample viscosity, standard injector settings had to be modified for injection consistency and reproducibility. Injector program was modified with a viscosity delay of 1 second and a sample wash and dispense speed of 300 ul/min. EEMPA injections were separated on a Restek Corporation (Belefonte, PA) Rxi-5ms 60m x 0.32 mmID x 1.0um film thickness gas chromatography column using a heat ramped gradient starting with an initial hold at 40°C for 1.0 minutes then ramping at 10°C/min to 200°C then 25°C/min to 320°C and held for 10 min for a total analysis time of 31.8 minutes. Full scan data was collected with m/z 44 and 18 ions extracted to produce the integrated peaks used for the quantification of carbon dioxide at ~2.27 minutes and water at ~2.51 minutes. The remaining chromatographic data was retained for further characterization of the EEMPA capture solvent. Samples were analyzed in triplicate to account for reproducibility of results.

Section S4: Process modeling and techno-economic analysis

Validation of the thermodynamic model

In this work, inter-laboratory data were collected from both PNNL and RTI international. Independent data validation was performed by PNNL, RTI, EPRI and Fluor. As observed from Figure S6(a) the VLE data measured by PNNL and RTI, marked by dots, agree with each other, while the current thermodynamic model developed using only PNNL's data, represented by the lines, can adequately describe all the data. The calorimetry data collected by RTI, as shown in Figure S6(b) indicates that the heat of absorption is around 75 kJ/mol CO_2, similar to the simulation results from Aspen Plus. Therefore, we can conclude that there is thermodynamic consistency established between calorimetry and VLE data. The current thermodynamic model can adequately describe the property data for process simulation and preliminary techno-economic analysis.

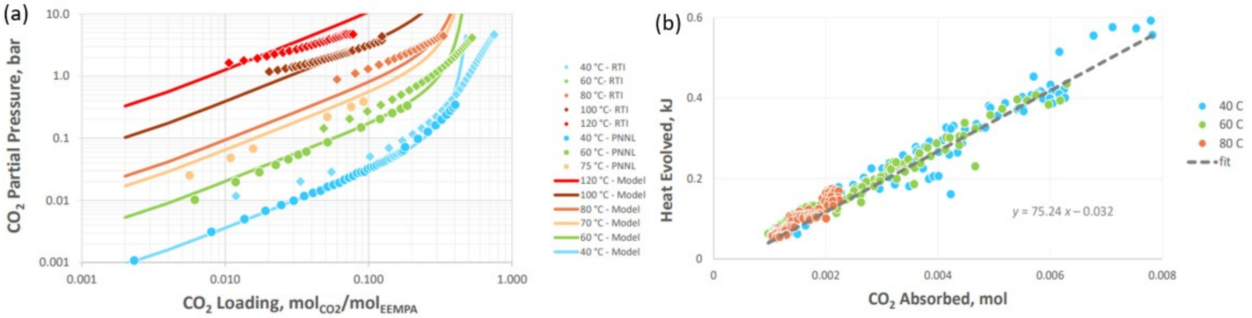

Figure S6. Validations of the thermodynamic model: (a) VLE, (b) Calorimetry data.

Detailed modeling results and cost projections for commercial scale plants

In this work, the approach recommend by National Energy Technology Laboratory (NETL) was used to evaluate the cost of CO_2 capture [2]. First, process models were developed for the entire supercritical coal fired power plant, including coal fired boiler, supercritical steam cycle, carbon capture unit, CO_2 compression, and cooling water system. In this model, the heat required for solvent regeneration is supplied by withdrawing steam from the supercritical steam cycle at the pressure level that can maintain a reasonable approach temperature of 5°C at the reboiler. The efficiencies and operating conditions of boiler, steam turbine and cooling tower were set the same as Case B12B in the NETL Rev2 report. For all cases, the plants were scaled to a net plant power output of 550 MW. Combining the mass and energy balance data from the Aspen Plus model, the capital cost projection of the carbon capture and compression units from APEA or EPC company, and the estimation on other auxiliary load and capital cost of non-carbon capture section reported by NETL, the cost of electricity (COE) can be calculated using NETL approach [2]. Next the cost of CO_2 capture can be calculated by **Eq. S2**. The equivalent work of carbon capture is calculated using the approach suggested by Lin and Rochelle [3] and the mass and energy balance of the carbon capture section reported by Aspen Plus. **Figures S7-S8** and **Tables S2-S3** provide detailed mass and energy balance, process configuration, and breakdowns of utility and cost reported in **Table 3**.

$$Cost\ of\ CO_2\ Capture = \frac{(COE_{CCS} - COE_{Non\ CCS})}{CO_2\ Captured}$$ (**Eq. S2**)

Table S2. Cost of carbon capture (Based on NETL Case B12B).

Solvent Configuration	Cansolv (Reproduced) LVC	EEMPA SS (SS316 packing in absorber)	EEMPA AHI/IHC/LVC (plastic packing in absorber)
Total (Steam Turbine) Power, kWe	641,583	638,044	648,277
Auxiliary Load Summary, kWe			
CO_2 Capture and Removal	16,000	10,483	20,503
CO_2 Compression	35,709	38,481	38,272
Non-Carbon Capture Units	39,666	39,158	39,225
Total Auxiliaries, kWe	91,375	88,122	98,000
Net Power, kWe	550,207	549,921	550,276
Net Plant Efficiency (%, HHV)	32.47	33.55	33.71
As-Received Coal Feed (kg/hr)	224,791	217,433	216,596
Thermal Input, kWt	1,694,369	1,638,908	1,632,599
Fuel Cost (¢/kWe-hr)	3.09	2.99	2.97
Total Capital Cost ($/kWe)			
CO2 Capture and Compression	1,149	1,166	943
Non-Carbon Capture Units	2,346	2,298	2,290
Owner's Cost	810	771	780
Capital Charge Factor	0.124	0.124	0.124
Capital Cost (¢/kWe-hr)	7.22	7.05	6.68
Variable Costs ($k/yr)			
CO2 Capture and Compression	8,093	2,765	2,724
Non-Carbon Capture Units	52,073	50,369	50,175
Variable Operating Cost (¢/kWe-hr)	1.47	1.30	1.29
Fixed Operating Costs (¢/kWe-hr)	1.54	1.49	1.48
Cost of Electricity* (¢/kWe-hr)	13.31	12.83	12.43
Cost of CO2 Captured ($/tonne CO_2)	59.0	55.6	50.6

*excluding costs associated with CO2 transportation, sequestration, and monitoring

Table S3. Equivalent work of carbon capture (kJe/mol CO_2 captured).

Solvent Configuration	Cansolv LVC	EEMPA SS	EEMPA AHI/IHC/LVC
Reboiler heating	25.7	19.1	15.1
Cooling	1.1	2.4	2.4
Refrigeration	0.7	0.7	2.0
Reclaimer heating	0.1	0.1	0.1
Solvent pumping	0.06	0.11	0.16
Compressing	12.4	12.8	12.9
Total	39.4	35.2	32.7

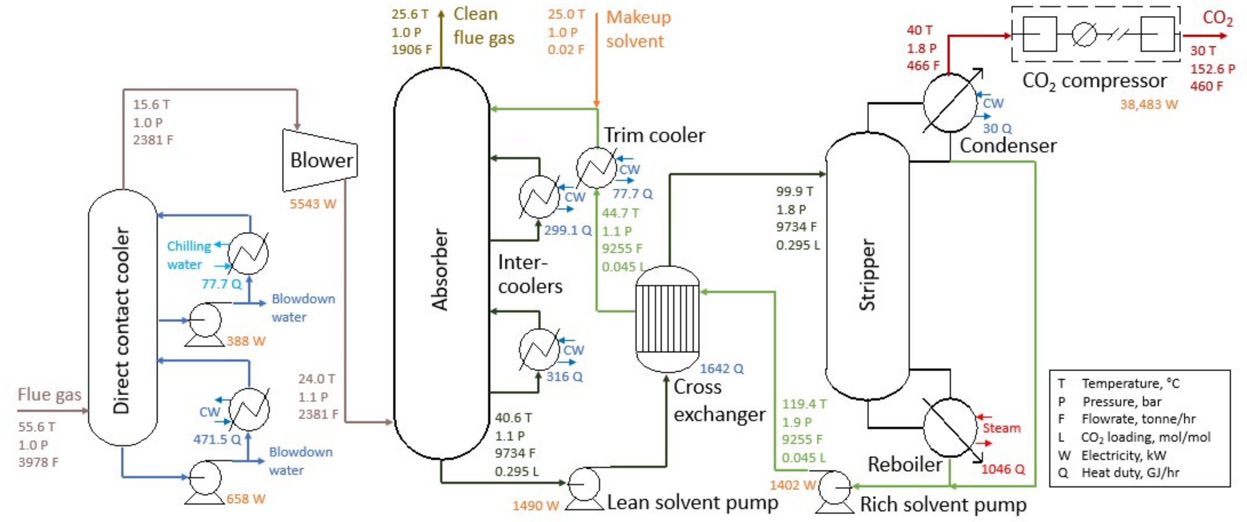

Figure S7. Mass and energy balance of EEMPA-based carbon capture unit with simple stripper configuration.

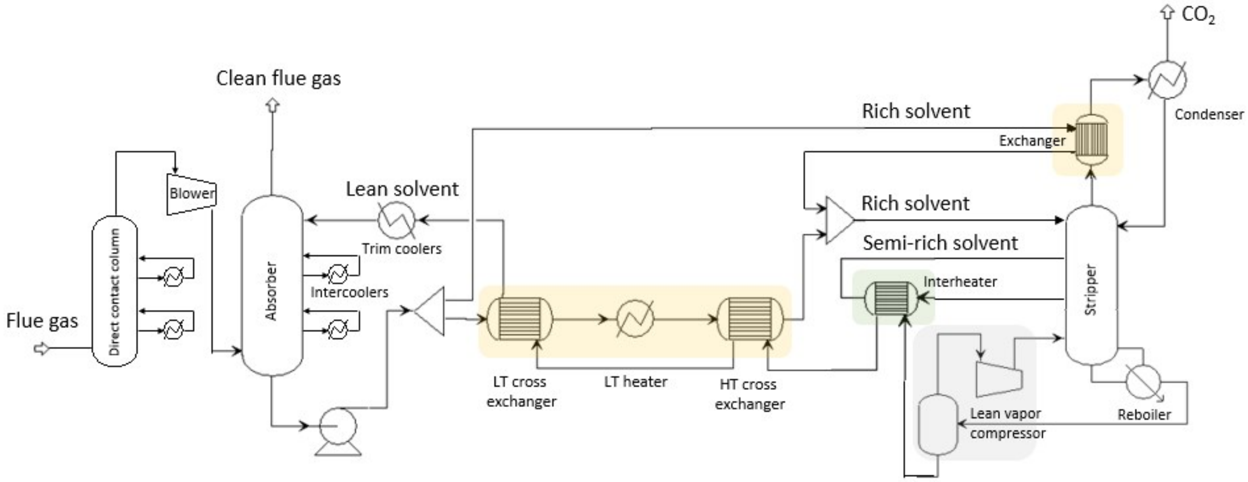

Figure S8. Process configuration of AHI/IHC/LVC.

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[3] Y.-J. Lin and G. T. Rochelle, Energy Procedia, 2014, 63, 1504-1513.