A systematic procedure for process energy evaluation for post combustion CO$_2$ capture: Case study of two novel strong bicarbonate-forming solvents.

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Abstract

Process simulation is used for energetic evaluation of two novel strong bicarbonate forming solvents for post combustion CO$_2$ capture, intended for coal- and natural gas based exhaust streams. An evaluation framework is devised where process energy sinks are coupled to process energy balances based on the basic principles of a thermal heat engine. This framework is then used to clarify where heat is spent in the process. The novel solvents here used, activated 2-Piperidineethanol (2-PPE) and 1-(2-Hydroxyethyl)pyrrolidine (1-(2HE)PRLD), in this paper referred to as HSA1 and HSA2, respectively, are compared with a base case of MEA and Cesar1. It is shown that HSA1 is the best performing solvent based on the given process setup. The regenerative efficiency parameter for HSA1 is 66% with an optimum specific reboiler duty (SRD) of 2.78 MJ/kg CO$_2$ removed, for a coal case, a 22% reduction compared to MEA. This results in a power plant specific energy penalty for avoided CO$_2$ (SEPAC) of 0.27 kWh$_{el}$/kg CO$_2$. These results are based on a traditional process setup, with no particular heat integration schemes. As shown using the evaluation framework, additional energy improvements can be realized by economizing configurations for improved internal heat distribution.

Highlights
• 	Energy evaluation of two strong bicarbonate-forming solvents applicable for post combustion CO$_2$ capture.
• 	A novel procedure for overall energy evaluation of CO$_2$ capture plants.
• 	Simulation to find optimum operation for CO$_2$ capture plants

Keywords
CO$_2$ capture, process modelling, solvent development, process optimization, thermodynamics

Nomenclature

α	CO$_2$ loading (mol CO$_2$/mol amine)
β_{CO_2}	CO$_2$ capture ratio (-)
C_{P_l}	Specific heat capacity liquid(MJ/kg K)
C_i	Molar concentration component i (mol/m^3)
$\Delta h_{vap,H_2O}$	Molar Heat of vaporization for water (J/mol)
$\Delta h_{ABS,CO_2}$	Molar solvent heat of absorption CO$_2$ (J/mol)
$H_{g,in}$	Enthalpy flow gas, into control volume (J/s)
ΔH_{Abs}	Solvent heat of absorption CO$_2$ (MJ$_{Th}$/kg CO$_2$)
$\Delta H_{Vap,H_2O}$	Heat of vaporization for water (MJ/kg)
H$_A$	Enthalpy at state A (or B) normalized to captured CO$_2$ (MJ/kg)
H$_{CO2}$	Enthalpy ideal gas CO$_2$ (MJ/kg)

$\frac{L}{G}$	Liquid-to-gas ratio (kg/kg)
M_i	Molecular weight for component I (kg/mol)
n_{eff}	Solvent regeneration efficiency (-)
ρ_l	Liquid Density (kg/m³)
Q_{Reb}	Reboiler duty (MJ$_{Th}$/kg CO_2)
Q_{ABS}	Absorption heat loss to surroundings (MJ$_{Th}$/kg CO_2)
Q_{Sens}	Solvent Sensible heat loss to surroundings (MJ$_{Th}$/kg CO_2)
Q_{strip}	Stripping heat loss to surroundings (MJ$_{Th}$/kg CO_2)
Q_{Ideal}	Thermodynamic ideal heat limit for regeneration (J/s)
Q_{Real}	The real heat requirement for regeneration (J/s)
R	Gas Constant (J/molK)
SRD	Specific reboiler heat duty (MJ$_{Th}$/kg CO_2)
T	Temperature (°C)
w_i	Weight fraction component i (-)
W_{Fan}	Fan work (MJ$_e$/ kg CO_2)
y_i	Molar fraction of component i, gas phase

Subscript

^	Indicating additional cooling sinks within control volume
Am	Amine
L	Lean solvent stream
R	Rich solvent stream
Sol	Solvent

1. Introduction

1.1 Background

The increased focus on carbon capture and storage (CCS) stems from the need to reduce CO_2 emissions from fossil fuel energy production as well as from industry, as described e.g. by the IPCC [1] and the IEA [2]. Success in achieving the goals, Norway and several other countries have set for CO_2 emission reductions requires implementation of large-scale CCS globally. This means that CO_2 must be captured from a wide range of sources in power generation and industrial activity, and transported to suitable storage sites. Post combustion capture with solvents is a robust technology and viable for large scale CO_2 capture from point sources such as power plants and industrial flue gases. In the past decade, with the increased focus on climate change, significant reductions in energy requirements have been realized in post combustion CO_2 capture technology. This has been accomplished by developing more energy efficient solvents as well as more energetically efficient process configurations for an overall improved capture process [1–9].

Significant work in the recent years has been conducted in finding ways of reducing the waste heat released by the CO_2 capture process as well as using the heat added to the process in a most efficient manner. State-of-the-art research on CO_2 capture with amines primarily follow two pathways, that is, solvent development and secondly, more energetically efficient process configurations.

In regards to solvent development, researchers have recently made progress in finding improved solvents for post combustion absorption from flue gases. Key characteristics are higher cyclic capacity, faster reaction rates for CO_2 absorption, lower heat of reaction, which in turn yields an overall lower thermal energy requirement for regeneration[10]. Several different amine solvents have been investigated, among them include blended amines and activated hindered amine systems [11–15]. Hindered amines do not form carbamates due to their steric hindrance around the nitrogen group, thus yielding a potential capacity of one mole CO_2 per mole of amine, contrary to primary and secondary amines, which form carbamates with a maximum capacity of only half a mole CO_2 per mole amine. The drawback is that these hindered amines usually have slow absorption rates or may have unfavorable vapor-liquid equilibrium (VLE) properties for low partial pressure CO_2 gases[16]. Mixed absorbents may therefore combine the increased equilibrium capacity of the tertiary bicarbonate forming amines, with the higher reaction rate of the primary and secondary carbamate forming amines. Blends of alkanolamines and polyamines may therefore provide tailored properties and consequently, the ratio of bicarbonate and carbamate is important for optimizing cyclic capacity versus acceptable absorption rates. Chowdhury et al. screened 24 tertiary amine absorbents, including three synthetic amines, with systematic modification of their chemical structures [17]. They report that seven tertiary amines have the potential to be used for CO_2 capture. Recently, Hartono et al. systematically tested fifteen bicarbonate forming solvents in a screening apparatus for classes of tertiary amines[18]. This resulted in identification of two solvent candidates, 2-Piperidineethanol (2-PPE) and 1-(2-Hydroxyethyl)pyrrolidine (1-(2HE)PRLD), with potential of much higher cyclic capacity than that for monoethanolamine (MEA), but with a significantly lower rate of absorption. For these candidates to be applicable for post combustion CO_2 capture, promotors/activators are needed to improve on the rate of reaction. Following this work, Hartono et al., screened several alkanolamines as possible activators[19]. The promotor, indicated as P4, was selected for further testing for VLE and heat of absorption measurements. These solvents, named HSA1 and HSA2, showed, from preliminary analysis by Hartono et al., a potential of very large cyclic capacities for both blends. Since the screening tests and the experimental data gathering only revealed preliminary information for these solvents, the next phase of work involves model development and simulation against benchmark solvent

technologies. In order to gain further understanding and determine process applicability of HSA1 and HSA2, the present study focuses on a detailed process simulation study of these novel blends.

The second common research pathway has been to look for ways of finding more energy efficient process configurations. A method often used for estimating thermal energy usage in this regard is to assess and compare the main contributing process heat sinks. To the best of our knowledge, there exists no procedure in the open literature that quantitatively compares rigorous process simulation with a thermal energy sink analysis that can be broken down and compared to simplified heat sink equations directly. The relationships between fundamental properties of the absorbent and the design of the absorption process, in view of the main process heat sinks, is discussed in Svendsen et al. [20], Oexmann et al.[7] and Neveux et al.[27]. Here, simplified equations for the main sinks are given. An elaborate derivation of variants of the Gibbs-Helmholtz equation, applicable to absorption processes, is given in Mathias [21]. It is here noted that process improvements are possible, while staying within the strict bounds imposed by the laws of thermodynamics. There have been numerous recent papers published on process optimization, simulation and changes in plant design for reducing the energy requirements of a post combustion capture plant, a thorough summary of recent papers up to 2016 is given in Feron [22]. Rochelle et al. [23], uses piperazine (40 wt%) in an energy analysis to assess process reversibility of post combustion capture processes, and a thermodynamic reversibility analysis is discussed by Yu-Jeng et al. [24], also for piperazine. Another superstructure-based approach using multiple process modifications was carried out by Oh et al. [25]. They report improved overall energy efficiencies with different process modifications, such as absorber intercooling and split-flow schemes. Damartzis et al.[26], have recently modelled different plant configurations based on specific characteristics of different solvents. They observed a 22% reduction in reboiler duty by utilization of an intercooled absorber configuration for a 30%wt MEA solvent. This is attributed to the enhanced equilibrium capacity shift towards the absorber bottom, however, it is not stated if the base case operated at an optimum loading level with respect to specific reboiler duty (SRD). Similarly, Sanpasertparnich et al.[28] report an improvement of 24.4% in SRD by using multiple absorber intercoolers, for quenching the evolving temperature bulge, also for MEA, reporting that an rich loading of 0.55 mol/mol is possible for their best intercooled case (for an 8.9 mol% CO_2 flue gas, at a bottoms solvent temperature of about 44°C), compared to a rich loading of 0.45 for their base case. Similarly, it is here not clear if the base case is optimized with respect to the solvent specific properties, or how close to equilibrium the rate based absorber reaches for the established base case. The need for a methodology for establishing where process improvements may be gained, that also differentiates where the major energy sinks are accrued, has been pointed out in a review article by Moullec et al. in 2014 [29]. This is especially helpful as many quantitative simulation studies are not supported by pilot plant data. The question raised is, whether, in performing quantitative process evaluations, one process modification showing a benefit over the other may be attributed to that particular change, or whether it is caused by a sub-optimized base case, that contain excessive heat sinks another place in the plant. A strict energy cost breakdown following from rigorous process simulations will help in identifying these sinks and may ensure correct interpretation of performance the various process units.

The primary objective of this work has been to implement simulation models into a flow sheet simulator for the two newly discovered solvents, HSA1 and HSA2, as screened and analysed by Hartono et al.[18,19] and subsequently investigate their potential for post combustion capture based on a simulation study. Additionally, the contributions of this work includes description and usage of an evaluation framework that incorporates the main process energy sinks to overall energy balances based on the principles of a thermal heat engine. This procedure enables coupling of detailed solvent properties, such as reaction enthalpy, VLE, and kinetics, with a quantitative overall process operation,

while correctly accounting for energy sinks in the process. This procedure also shows where there may be room for further improvement in the process, and illustrates how the fundamental chemical properties of the solvents give rise to the overall capture potential and how the major energy sinks in the process are mutually dependent of each other. An investigation is thereafter made by comparing the thermodynamic efficiency of the overall process, using the HSA1 and HSA2 solvents, benchmarked against conventional MEA as well as the formulated Cesar1 solvent.

For the purpose of the process comparisons and evaluations of the solvents, a comparison is in its simplest form investigated without the rest of the power plant. Therefore, a control volume has been placed across the capture process only, to investigate the thermal energy demand for solvent capture and regeneration. In this way the input exhaust gas is specified, and the energy required for the set capture rate at a given desorber pressure is given by the simulations. As the capture process is an interacting part of the rest of the power plant, and should be viewed as a part of the overall power production plant, the solvents performances are finally presented in an overall process simulation, including the compression train and power island, so that the overall work may be quantified. The overall specific loss in power output for a given power plant, the energy penalty for avoided CO_2 (SEPAC), is then assessed.

2. Theory

2.1 Establishment of thermodynamic framework and clarification of concepts

The heat consumption, i.e. the thermal energy required for CO_2 absorption followed by solvent regeneration, involves the largest cost associated with the overall capture process and accounts for around 80-90% of the overall operational costs when not considering the subsequent CO_2 compression stages. The following describes a framework that enables accurate separation of the different energy sinks in the process.
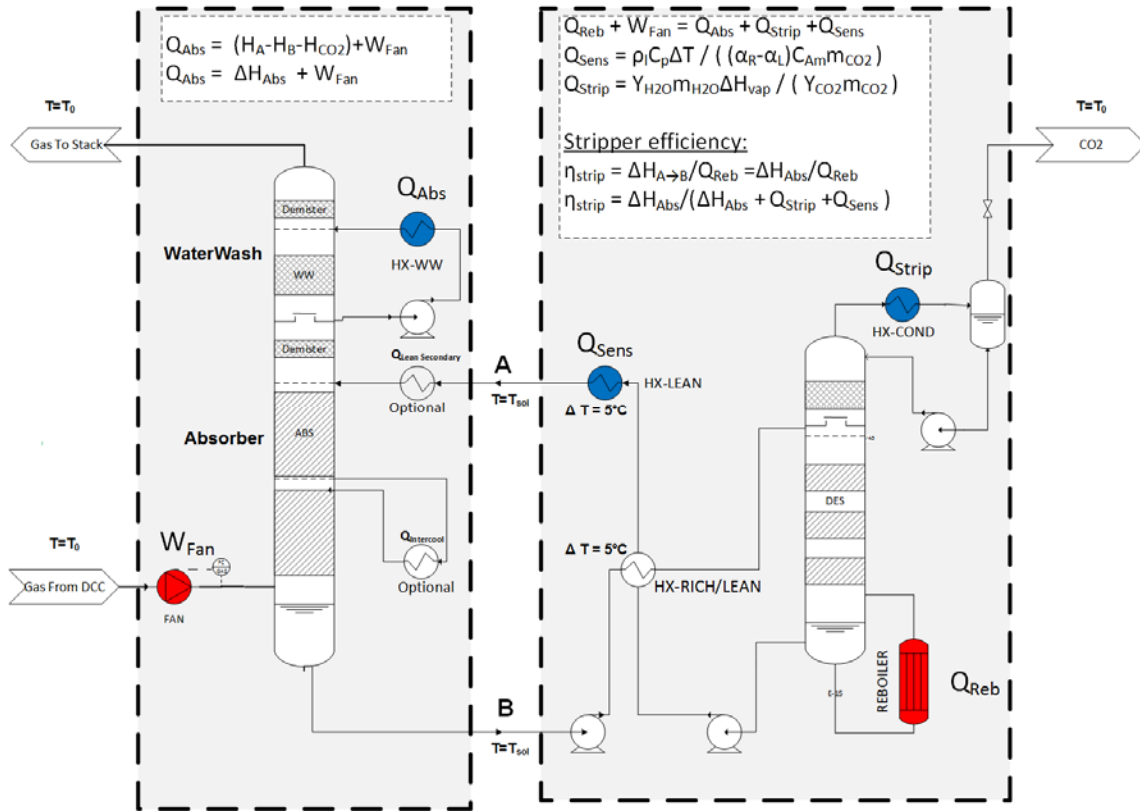
Figure 1: Flowsheet with main heat sinks (blue) and sources (red), liquid pumps are not considered.

A generic post combustion absorption process is illustrated in Figure 1, where exhaust gas is transported from the upstream DCC (direct contact cooler) to the absorber by a fan/blower. The exhaust gas and a liquid solvent flows counter-currently over a packing material through the absorber.

The thermal swing CO_2 absorption process can be thought as *a thermal heat engine* i.e. it needs a hot and cold reservoir. However, the output or product from this absorption heat engine is solely concentrated CO_2 at moderate pressure in contrast to the common thermal Rankine cycle, which can produce or yield an output of mechanical work. Thus, the enthalpy balance for the absorption heat engine can be simplified to:

$$Q_{Hot\ reservoir} + Work\ In \cong Q_{Cold\ Reservoir} \qquad (1)$$

This estimate is based on a neutral water balance e.g. no water vaporization to the surroundings. The enthalpy balance can be further decomposed to:

$$Q_{Reb} + W_{Fan} \cong Q_{Abs} + Q_{Sens} + Q_{Strip} \qquad (2)$$

Where the main heat source, Q_{Reb}, is the total reboiler duty and the W_{Fan} is the added work by the fan. The work from solvent pumps are in this framework neglected. The main heat sinks are the sensible heat loss in the lean trim cooler (Q_{Sens}), the stripping steam loss into the desorber condenser duty (Q_{Strip}) and the solvent heat of reaction loss found from the absorber water-wash cooler (Q_{Abs}). This is illustrated in Figure 1, which shows the absorption/desorption flowsheet with the main heat sinks and sources. Hence, as shown from equation 2, optimizing the absorption process to obtain the minimum reboiler duty is equivalent to minimizing the cooling duty or cooling water demand to the process. These heat sinks represent the irreversible (this term will be discussed in more detail later in the paper) energy losses to surroundings, or in another context, the total heat transferred to the cooling water.

The local heat balance around the absorber control volume is also illustrated in Figure 1 where CO_2 rich exhaust gas flows into the absorber and CO_2 depleted exhaust gas flows out, while lean solvent flows into absorber top (at state **A**) and CO_2 rich solvent (at state **B**) flows out of the absorber. The global water balance can only be zero if there is no net gain or loss of water from the exhaust gas, thus, the outlet gas (dewpoint) temperature must be approximately equal the dewpoint temperature for the gas inlet i.e the DCC temperature. Furthermore, the enthalpy flow into the control volume from the gas flow that is not participating in the absorption, that is, water vapour and inerts and the rejected (amount of not captured) CO_2 in the gas inlet, are approximately equal to the gas outlet enthalpy flow from the control volume. This is a valid approximation if the gas can be treated as ideal, which is usually the case at ambient operating pressure. In other words, the enthalpy change for the gas stream is reduced to loss of the ideal gas enthalpy of CO_2 absorbed. For the solvent, the temperature is equal for both the inlet and outlet (state **A** and **B**), thus there is no sensible heat contribution to the control volume. The lean solvent can be cooled beyond state **A** to a lower temperature. However, first it is assumed only lean cooling to state **A.** Additional lean cooling and intercooling will be addressed later. The solvent temperature (T_{sol} in Figure 1) is then at the adiabatic absorption saturation temperature, as determined by the given thermodynamic/mass transfer relation. The enthalpy balance for the absorber control volume can then based on the given assumptions be expressed as:

$$accumulation = In - Out + Source \qquad (3)$$

$$0 = (H_A - H_B)_{T=T_{sol}} + (H_{g,in} - H_{g,out})_{T=T_0} + (W_{Added} - Q_{Abs}) \qquad (4)$$

$$0 \cong (H_A - H_B) + H_{g,CO2\ Captured} + (W_{Fan} - Q_{Abs}) \qquad (5)$$

$$Q_{Abs} \cong \Delta H_{Abs,CO2} + W_{Fan} \qquad (6)$$

Where H_g is the gas enthalpy to the exhaust gas, Q_{Abs} it the cooling duty for the absorber water wash and ΔH_{Abs} is the CO_2 absorption heat at $T = T_{sol}$. That is, the heat generated by added work and CO_2 absorption can only escape the absorber control volume through cooling in the water-wash sections (Q_{Abs}) under the constraint that the water balance is closed and that the lean solvent is not subcooled below the rich solvent temperature (T_{sol}). Thus, in post combustion absorption processes, the absorber water-wash is by all practical means also operating as a condenser, and furthermore, the absorber condenser has actually a significantly larger cooling demand than the desorber condenser. Consequently, solvents with low volatility, e.g. amino acids salts, can thus not omit the water-wash in the absorber due to the cooling required for water vapour condensation. Such units are still needed for returning condensate to the process and maintaining water balance. This important consequence can be illustrated with an example: The heat of absorption for a 30 wt% MEA solvent is approximately 85 kJ/mol CO_2, or 1.93 MJ/kg CO_2 absorbed. The specific reboiler duty for this process is about 3.6 MJ/kg CO_2 at 90% CO_2 capture. Hence, for a generic MEA absorption process without economizing configurations, more than 50% of the total reboiler duty is "lost" into the absorber "condenser", given by the cooling requirement. This also reveals the thermodynamic limitation for an absorption process, which is such that the minimum energy to reverse the absorption process can never be lower than the non-recoverable loss of the heat of absorption itself. Thus, a hypothetical perfectly reversible desorption process will, as an absolute minimum, require the absorption enthalpy replenished in the regeneration process. This is the case for any thermal swing regeneration process, even for most non-thermal regeneration processes. As an exception, a heat pump could be applied to transport the absorption heat to the regeneration section, however the quality of the absorption heat will be very

low (low temperature). A pressure swing (direct contact heat pump) regeneration process could also potentially conserve the heat of absorption, but an expensive vacuum below 1 kPa would be required in a post-combustion pressure swing process. Thus, in practice, the absorption heat is generally irreversible lost into the heat sinks in post-combustion. This is an important and often misunderstood fact and states that any classic heat integration (not including heat pump or pressure swing schemes), will not be capable of recovering the released heat of absorption term.

2.2 Process reversibility

Following from the above discussion, the minimum heat/enthalpy demand to regenerate the solvent from state **B** to state **A** in Figure 1 is thus equal to the CO_2 absorption heat, and one may define an overall regeneration efficiency, which is the minimum or ideal heat requirement for regeneration of the solvent divided by the actual or real heat demand. As mentioned earlier, the overall heat evolved in the absorber (Q_{Abs}), equals the exothermic reaction heat plus the heat input from the fan. Other sources of mechanical work such as liquid pumps are neglected in this thermal analysis as they are small. The following approximates the efficiency as the specific solvent heat of absorption divided by the total thermal energy per unit CO_2 removed, the SRD.

$$n_{eff} = \frac{Q_{Ideal}}{Q_{Real}} \tag{7}$$

$$n_{eff} = \frac{Q_{Abs} - W_{Fan}}{Q_{Reb}} \cong \frac{\Delta H_{Abs}}{\Delta H_{Abs} + Q_{strip} + Q_{Sens}} = \frac{\Delta H_{Abs}}{SRD} \tag{8}$$

For the generic MEA solvent example above the thermal regeneration efficiency is then: $n_{eff} = \frac{1.93}{3.60} = 53\%$. That is, the thermal regeneration of the MEA solvent has approximately 50% loss of overall SRD due to steam loss into the condenser (Qstrip) and due to sensible heat that is lost in the lean-rich cross heat exchanger. As an example, in the Cesar project [30], the use of Lean Vapor Recompression (LVR) reduced the SRD from 3.6 to 3.1 MJ/kg for MEA, thus, the thermal efficiency was then increased to 1.93/3.1=63% . The compression work required for LVR may be significant, and has not been included into the SRD calculation above. This explains why LVR can be effective for MEA, simply because the potential for efficiency improvement is greater than for solvents requiring less steam for regeneration. The Cesar1 solvent, a solvent that already requires much less steam for regeneration, did not see this improvement. This solvent already employs the same efficiency gain though through better solvent characteristics. If a solvent system achieves 75-80% thermal efficiency ($n_{eff} = 75 - 80\%$), then the SRD requirements will be 2.4-2.6 MJ/kg CO_2 assuming that heat of absorption is close to the solvents studied in this work. Thus, a generic post-combustion absorption process, with no particular process optimizations or economizing configurations, such as many generic pilot-plants, will have a thermodynamic limit at approximately 2.5 MJ/kg CO_2 or more precisely 5/4 of the absorption heat. Further improvements beyond this limit will require improved internal heat exchanging and redesign of the absorption process. Thus, there is little room for improvement by minimizing steam and sensible heat requirements further and innovations thus need additional focus on the given process configuration, in addition to the absorption process itself. Improved internal heat exchanging of the process, beyond the generic scheme, as shown in Figure 1, has not been the focus of this paper, but will be addressed in a follow-up paper.

From this it can then be pointed out that any attempt to alter the process cooling sequences in the absorber section will not reduce this heat of absorption. For example, the lean solvent is sometimes cooled additionally below T_{sol} and/or absorber intercoolers are added to the absorber column. If an additional cooler, inter-cooler or other form of cooler unit is added to the lean solvent stream, or any

other place within the absorber control volume as shown in Figure 1, a modification to the enthalpy balance must also be added. This can be thought of as adding a secondary cooling unit, which reduces the solvent temperature from T_{sol} to T_{Lean} or any temperature reduction inside the control volume. The new enthalpy balance becomes:

$$\hat{Q}_{Abs} + \hat{Q}_{Lean\ secondary} + \hat{Q}_{Intercool} = Q_{Abs} \tag{9}$$

$$\hat{Q}_{Abs} + \hat{Q}_{Lean\ secondary} + \hat{Q}_{Intercool} \cong \Delta H_{Abs} + W_{Fan} \tag{10}$$

Where $\hat{Q}_{Abs}$ is the new water-wash cooling duty with the additional solvent cooling or intercooling units. Additional cooling only internally moves a fraction of the original cooling duty (Q_{Abs}) from the original water-wash section to the new cooling units inside the absorber control volume. The net cooling demand, or irreversibility, is still the same and limited by the reaction enthalpy of the solvent. The same argument holds for any type of absorber cooling or heat integration. On a more positive side, absorber intercooling and other schemes potentially has a thermodynamic effect by altering the average driving forces through the absorber and may subsequently increase rich loading and thus cyclic capacity. This potential improvement may only reduce the sensible and stripping steam requirements, as will be discussed below and shown in equations 13 and 14. Thus, this thermodynamic analysis shows that the heat of absorption released as well as any added work (equation 10) in the absorber control volume is irreversibly lost to the internal heat sinks e.g. water-washes, lean-coolers or intercoolers.

The total accumulated energy sinks around the plant control volume will thus equal the input reboiler duty, as we consider the plant with no surrounding heat losses. An energy sink breakdown can be performed to determine where the energy usages are located. This understanding will help in determining energetic potentials of a process as well as the potential of the solvent. Approximations of these energy sinks have been presented frequently in literature, for example in [20].

These sinks can be referred to as: 1, the exothermic reaction energy (Q_{Abs}), 2. The steam required to provide a sufficient driving force in the stripper and reboiler (Q_{Strip}), and 3, the sensible heat loss (Q_{Sens}) in the thermal swing.

The overall heat balance per kg CO_2 captured is thus usually formulated as:

$$Q_{Reb} \cong Q_{Abs} + Q_{Sense} + Q_{Strip} \tag{11}$$

$$Q_{Abs} = \Delta H_{Abs} \tag{12}$$

$$Q_{Sens} \cong \frac{\rho_{Solvent}\ C_{P_{Solvent}}\ \Delta T_{Lean}}{M_{m,CO_2}\ C_{Amine}\ (\alpha_{Rich} - \alpha_{Lean})} = \left(\frac{L}{G}\right) * \frac{C_{P_{Solvent}}\ \Delta T_{Lean}}{w_{CO_2,gas\ in}\ \beta_{CO_2}} \tag{13}$$

$$Q_{Strip} \cong \left| \frac{y_{H_2O} M_{m,H_2O}}{y_{CO_2} M_{m,CO_2}} \Delta H_{Vap,H_2O} \right|^{T=T_{Stripper\ top}} = \left| \frac{w_{H_2O}}{w_{CO_2}} \Delta H_{Vap,H_2O} \right|^{T=T_{Stripper\ top}} \tag{14}$$

Where y_i, w_i, $M_{m,i}$, C_i and $\Delta H_{Vap,i}$ are; the mole fraction, weight fraction, molar mass, molar concentration and heat of vaporization for component i. Furthermore, the $w_{CO_2,gas\ in}$, α, β_{CO_2}, $\frac{L}{G}$ and $C_{P_{Solvent}}$ are the weight fraction CO_2 in the exhaust gas absorber inlet, the molar CO_2 loading [mol CO_2/mol amine], the CO_2 capture ratio, the Liquid-to-Gas mass ratio and the specific mass heat capacity of the solvent, respectively.

The first heat sink (ΔH_{Abs}) is as noted purely dependent of the solvent characteristics. Properties as primary, secondary, tertiary amine can be important factors as well as the dissociation constant and carbamate stability if the solvent is alkolamine based. Based on equation 11, the heat of absorption should preferably be as low as possible, however, the three sinks or equations are not independent of each other. A too low heat of absorption will have adverse effects on the two other sinks. This is described in section 5 for the investigated solvents. A reference article on this topic can be found here [31].

The second heat sink (Q_{Sense}) is the approximate sensible heat loss due to the thermal swing encountered in the process. There is always some sensible heat losses due to loss of thermodynamic availability in the process, i.e. the lean-rich cross heat exchanger is never 100% efficient, thus a fraction of the heat added in the reboiler escapes or slips through to the cold side in the cross-flow heat exchanger. The heat sink is proportional to the temperature approach in the lean-rich cross-exchanger, the heat capacity of the solvent and liquid-to-gas ratio. The weight fraction of CO_2 in the absorber inlet and the capture ratio is fixed in equation 13. It is shown that it is clearly beneficial to have a solvent with high cyclic capacity of CO_2 and low heat capacity. Increasing heat transfer area reduces the temperature approach at the expense of increased capital expenditures (CAPEX). Other factors that may influence the overall heat transfer coefficients, such as lower solvent viscosity, increased turbulence etc., will also improve heat exchanger performance and thus lower Q_{Sense}.

The last heat sink (Q_{Strip}), equation 14, is rigorously found by simulation or estimated by the heat requirements to produce the stripping steam out of the stripper overhead. It is in the estimation assumed that the latent heat of vaporisation of water is dominant and the sensible heat to the gas is negligible i.e CO_2 and water are assumed as the main gas components. Vaporization of the solvent components are assumed negligible, as the solvent vapour pressure is usually an order of magnitude lower relative to water. This sink is very important together with the sensible heat sink, as discussed above, these are the only sinks that one can reduce based on process improvements which may improve thermodynamic driving forces in the process. Higher equilibrium pressure of CO_2 and lower partial pressure of steam will reduce this heat sink, as shown with the following example. Often the equilibrium partial pressures of CO_2 and H2O are higher than the overall pressure in the hot inlet fed to the stripper leading to flashing and subsequently lowering of the equilibrium pressures. This flashing does in fact reduce the overall potential to reduce Q_{Strip}. That is, Q_{Strip} would be lowest or at a minimum if the hot solvent was fed to the stripper exactly at its bubble-point temperature. However, this cannot happen (with a typical process flow scheme) without lowering the hot rich temperature to the solvent cross exchanger, and subsequently increasing sensible heat loss (Q_{Sense}). For example, due to flashing, a solvent heat exchanger with 1kW improved heat transfer will not reduce the overall reboiler duty to the same extent, but rather closer to 0.5 kW. This occurs because some of the improved heat transfer of 1 kW will be wasted to increased flashing, unless process specific changes are implemented to prevent this, because of the increased steam to CO_2 ratio ($\frac{y_{H_2O}}{y_{CO_2}}$) as given in eq. 14.

One may ask why rigorous simulation is necessary, and why the approximate energy sink equations may not be sufficient in describing the process heat requirements. The basis for arriving at the approximate energy equations do not consider rigorous thermodynamic and rate descriptions, such as temperature and compositional dependence on species activities and its dependence on the solvent heat of reaction. It also does not consider hydrodynamic factors pertinent for the columns and its dependence on driving forces along the packing sections. The underlying models in the process simulator thus handle the specific solvent properties and process configurational effects, and are thus

separated from the overall energy analysis. The methodology used here can therefore be a valuable tool in particular for investigating new solvent systems, and even "hypothetical" solvents.

With the given basis framework with utilization of the same rules established in this section, these approximated equations for the energy sinks can be identified directly based on rigorous process simulation. In the following, three solvents are investigated by obtaining the cooling requirements around the control volumes based on the procedure described.

3.   The reference capture plant and basis for simulation

For the simulation work, the CO_2SIM software is used. CO_2SIM is an-in house software package that is developed at SINTEF/NTNU [32]. In Figure 2 is shown a flow diagram of the base case plant as simulated in CO_2SIM. It has a conventional process structure. The base case includes a direct contact cooler (Humidifier), a flue gas fan and a water wash (shown as a simple cooler unit) that recycles the condensed water back to the rich stream.
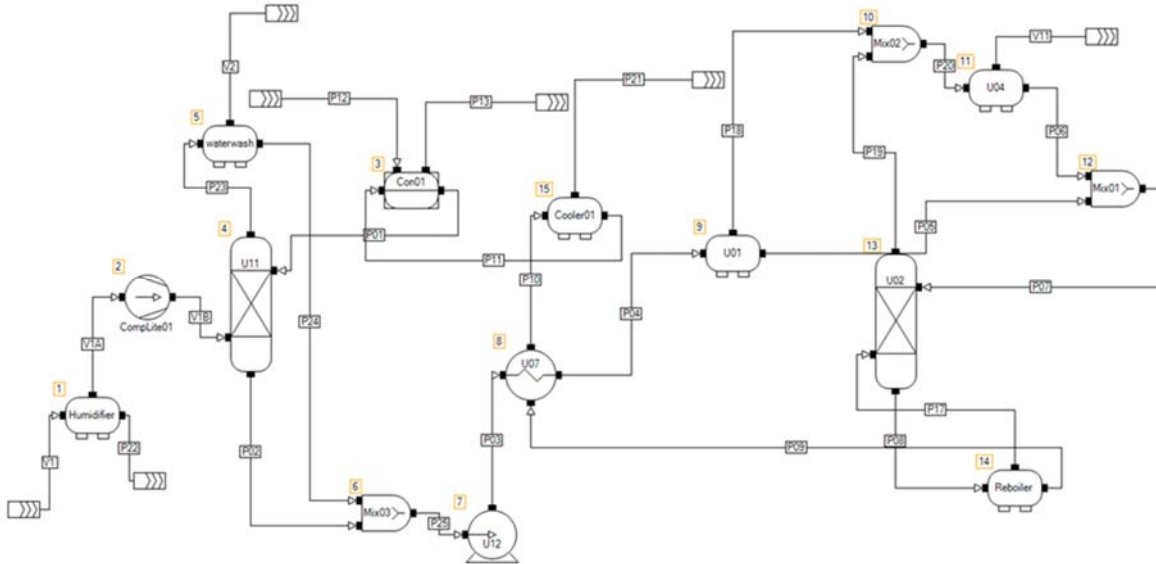

Figure 2: Simplified illustrative flowsheet of the reference plant configuration used in the study. Representation generated from the CO_2SIM software.

The base case process setup as well as unit sizes have been determined from a standardized case as defined in the "European best practice guidelines for assessment of CO_2 capture technologies", as part of the CESAR project [33]. It resembles a full scale CO_2 capture plant from a coal fired plant. The pulverized coal fired power plant has a net electric output of 800MW and includes a desulfurization unit prior to the CO_2 capture plant. The specific inlet flue gas composition for the flue stream (V1) is given in Table 1. More information about the base case can be found elsewhere [34].

The absorber and desorber were set to given column heights, whereas the heat exchanger is defined based on a temperature approach. This simulation analysis concerns energy analysis and does not focus on other solvent properties such as degradation and emissions. However, a reboiler temperature constraint is given such that it never exceeds 126°C, by setting the reboiler pressure to 205kPa for all simulations. As noted, the compression train is not included in this direct comparison, but included in the overall work analysis in section 5.7. Optimization is performed using an optimization utility function in CO_2SIM. The optimization routine changes defined operational and design parameters or variables, such as circulation rate, to minimize reboiler heat duty at given process constraints; in this case the capture efficiency defined as a percentage CO_2 flue gas removal. Thus, optimum loading ranges and circulation rates with respect to minimum reboiler duty can be found by defining the CO_2 capture degree, which is in these simulations is set to 90%$_{vol}$.

In the following simulations, the separation of energy sinks are done by a special defining of the lean cooler Cooler01 in Figure 2(or HX-LEAN in Figure 1), to ensure that the rich solvent temperature out of the absorber equals the inlet temperature. This is done by setting the input solvent cooler to a temperature reduction equalling the heat exchanger temperature approach, which is set to 5°C.

$$T_{absorber\ inlet} = T_{absorber\ outlet} \rightarrow \Delta T_{lean\ cooler} = \Delta T_{Hex\ Approach} \quad (15)$$

Where $T_{solvent\ inlet}$ yields the correct inlet solvent temperature to the absorber, ensuring close to adiabatic conditions across the absorber control volume. Secondly, the water wash temperature is adjusted to be equal the inlet saturated gas temperature.

The main assumptions for the comparative simulations are that the compression train is not included, the cross flow heat exchanger is defined on an a heat approach defined on the cold side to 5°C, and the column diameters are set so that the gas velocity does not surpass 70% of flooding.

4. Implementation of solvent models

The developed models for the solvents HSA1, HSA2 and Cesar1 are based on experimental data and correlations, e.g. chemical equilibria, heat of reaction measurements, viscosity and density measurements. HSA1 and HSA2 are two activated solvents developed in the HiperCap project (2014-2017), which is a 7th framework programme of the European Commission [35]. The Cesar1 solvent is a novel blend developed in the Cesar project [36]. All solvent models are implemented using the same process setup, and with the same code framework, which makes benchmark comparisons easier and minimizes systematic errors. The main data used in describing the solvents are described in [19]. Implementation practices and models used, as well as a description of the MEA model, are described in more detail in [37]. The obtained VLE- and heat of reaction data was used as well as specific density and viscosity models were used based on experimental data also from Hartono et al. All other necessary models, such as other physical property models and packing correlations are based on earlier work, or if not available, approximated based from literature data, see also reference [38]. Detailed description of the model implementation and assumptions of the "soft-model" approach in CO_2SIM is not given in further detail here, but can be obtained by contacting the authors.

In regards to chemical kinetics, emphasis has been placed on developing procedures for rapid understanding of a solvents potential for post-combustion CO_2 capture. Therefore, priority has been put on obtaining quality VLE data before detailed kinetic data. The HSA1, HSA2 and Cesar1 systems are promoted with an activator to enhance absorption kinetics, and screening measurements show that the systems have sufficient kinetics to allow for a normal sized absorber for coal capture [19]. The simplified kinetic model is based on an enhancement factor model as described in [39].

Table 1: Inlet base case flue gas composition (prior to the DCC indicated as Humidifier)

Flue gas (kg/h)	2 859 330
Flue gas (kmol/h)	98 016
Flue gas Temp. [°C]	47
Flue gas Press [kPa]	105
CO_2 at inlet (mol% wet)	13.6
H_2O at inlet (mol% wet)	10.2

5. Results and discussion

5.1 Optimum operation for the solvents for the reference plant

By varying circulation rate and keeping the CO_2 removal constrained to 90% for the given configuration, optimums were found for the standard base case flow sheet with respect to specific reboiler duty (SRD) for all solvents. The results for the four different solvents, SRD versus liquid/gas ratio (L/G), are shown

in Figure 3. The individual energy balances over the different unit operations are compared with the specific reboiler duty input and fan duty specification. A summary of the most important process results is given in Table 2. The absorber packing height is set to 16.5 m as default for MEA and Cesar1, however, HSA1 and HSA2 have been given absorber heights of 24 m, as these two solvents are slower and require higher packing sections for adequate capture. The Cesar1 solvent is simulated with heights of both 16.5 and 24 meters.
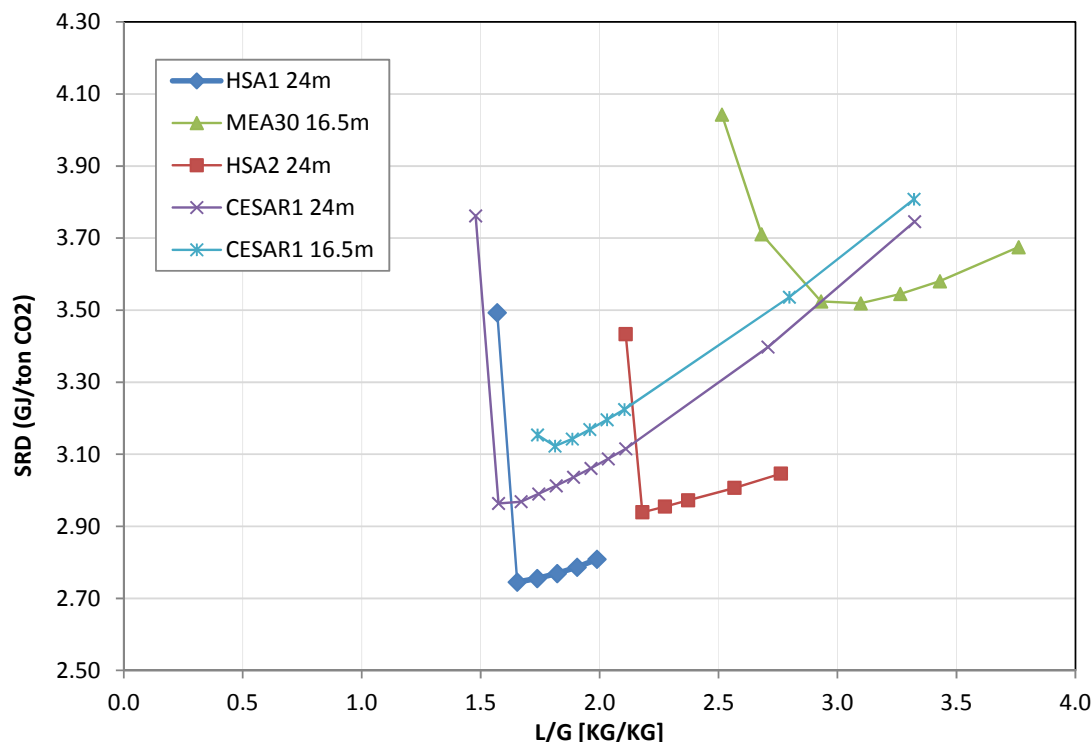

Figure 3: SRD [MJ/kg CO_2] versus L/G [kg/kg] ratio for the solvents under investigation

Table 2: Summary data for the solvents under investigation

Optimum run	Cesar1 16.5m	Cesar1 24m	HSA1 24m	HSA2 24m	MEA 16.5m
Absorber					
Packing height [m]	16.5	24	24	24	16.5
Column diameter* [m]	18.2	18.2	18.2	18.2	18.2
Solvent lean flow rate [kg/s]	1498	1251	1314	1731	2460
Solvent lean CO_2 loading	0.09	0.08	0.04	0.02	0.20
Solvent rich CO_2 loading	0.62	0.68	0.64	0.42	0.49
Flue gas [KNm3/h]	2204	2204	2204	2204	2204
Flue gas temp. [°C]	47	47	47	47	47
Flue gas press. [kPa]	105	105	105	105	105
CO_2 at inlet [mol %wet]	13.60	13.60	13.60	13.60	13.60
H_2O at inlet [mol %wet]	10.16	10.16	10.16	10.16	10.16
CO_2 recovery [%]	90	90	90	90	90
CO_2 captured [ton/h]	528	528	528	528	528
Stripper					
Packing height [m]	10.0	10.0	10.0	10.0	10.0
Column diameter [m]	10.4	10.4	10.4	10.4	10.4
Reboiler press. [kPa]	205	205	205	205	205
Reboiler temp. [°C]	124	124	125	126	122
Condenser temp. [°C]	30	30	30	30	30
Reboiler duty [MW]	458	435	403	431	516
Specific Reboiler duty (SRD) [MJ$_{th}$/kg CO_2]	**3.12**	**2.96**	**2.75**	**2.94**	**3.52**

Specific solvent requirement [kg solvent/kg removed]	9.81	8.53	8.95	11.80	16.78
Cross flow hex rich inlet temp. [°C]	46	46	46	47	48
Cross flow hex rich outlet temp. [°C]	116	113	112	113	116
Cross flow hex lean inlet temp. [°C]	124	124	125	126	122
Cross flow hex lean outlet temp. [°C]	51	51	51	52	53
Temperature difference cold side [°C]	5	5	5	5	5
Temperature difference hot side [°C]	8	11	13	12	6
Liquid/Gas [kg/kg]	1.81	1.57	1.65	2.18	3.10

*based on required volume applicable for one single train

As can be seen from Table 2, the optimum for HSA1, HSA2 and Cesar1 shows lower SRD's compared to MEA with values of 2.75, 2.94 and 2.96 MJ/kg CO_2 respectively, compared to 3.52 MJ/kg CO_2 for the reference case with MEA.

For solvent HSA1 with a 24-meter absorber column, optimum L/G ratio is 1.65. The approach to equilibrium based on loading level reaches 90% in the absorber, and based on CO_2 partial pressures, an approach of 55% at the bottom of the absorber. The lean loading level for the optimum is low, 0.04 mol/mol, which indicates that the solvent is readily regenerated by stripping steam. The solvent also produces the largest CO_2/H2O ratio at the top of the stripper column of the solvents. The rich loading level is 0.64, yielding a loading difference of 0.6, and a cyclic capacity of 113 g CO_2/kg solvent. The total reboiler heat duty is 402MW$_{th}$.

For solvent HSA2, with a 24-meter absorber column, the optimum at an SRD of 2.94 MJ/kg yields an L/G ratio of 2.18 kg/kg. The absorber reaches a degree to equilibrium based on loading level of 91% at the bottom of the absorber, and based on CO_2 fugacities 61% at the bottom of the absorber. According to the simulation, it is possible to reach a lean loading level of around 0.02 before reaching the steam break through and there is still some driving force at the absorber top liquid entrance for 90% CO_2 capture. The rich loading for this case is 0.42 giving a loading difference of 0.40 and a cyclic capacity of 86 g CO_2/kg solvent. The lean loading level for the optimum is thus very low for both HSA1 and HSA2 solvents, and pinching (the point at which driving forces approach zero) at the top of the absorber may become limiting at high degrees of capture.

The Cesar1 solvent was found to have an optimum SRD of 2.96 for the 24-meter absorber and 3.12 for the 16.5m absorber. The lean and rich loadings at optimum was found to be 0.08 and 0.68 for the highest absorber, yielding a loading difference of 0.60 and the highest measured cyclic capacity of 118 g CO_2/kg solvent.

These overall SRD values are all significantly lower than for the optimum reference case for MEA 30wt%, which has a cyclic capacity of 60 g CO_2/kg solvent. With the increased cyclic capacity, these systems can be operated with much lower circulation rates compared to MEA.

5.2 Analysis of the process heat sinks

In Figure 4 and Figure 5, the optimum runs based on minimum thermal duties and SRD are shown respectively, with breakdowns of the overall plant cooling duties. With basis on the framework described in section 2, the energy sinks are broken down for the best performing runs. As shown by the rigorous modelling of the process (after performing the heat-sink-separation procedure), the approximation given in eq. 11, by dividing into the given energy sinks, match almost exactly.

5.2.1 Absorber Energy loss
As expected, it is shown in Figure 4 and Figure 5 that that largest energy sink encountered in a CO_2 absorption process occurs in the absorber, due to the unrecoverable heat production from the exothermic chemical reactions. As discussed in section 2, this part of the overall reboiler duty is

released as water vapor at the top of the absorber and cannot be recovered with the given process setup. The temperature of the water vapor has low thermodynamic value, usually between 40-75°C. As shown in the figure, this irreversible energy loss is for HSA1, as this is the most energetically efficient solvent, 66% of the total reboiler duty (Q_{Abs}, Eq. 12). For the remaining SRD, 28% is spent in the solvent regeneration section to provide driving force (Q_{Strip}, as approximated in Eq.14), and 6 percent is spent at the lean cooler unit (Q_{Sens}, as approximated in Eq.14), due to the penalty incurred in the cross flow heat exchanger. It is shown that although the absorption heat for the HSA1 is only marginally smaller than for 30 wt% MEA, the overall SRD is significantly lower.
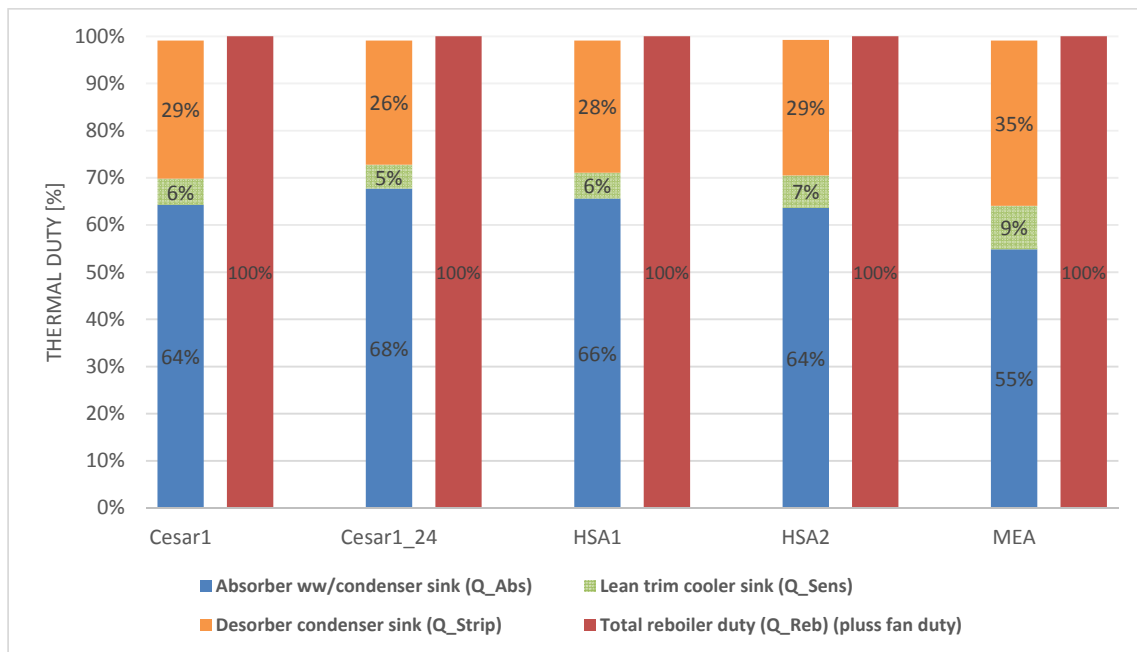
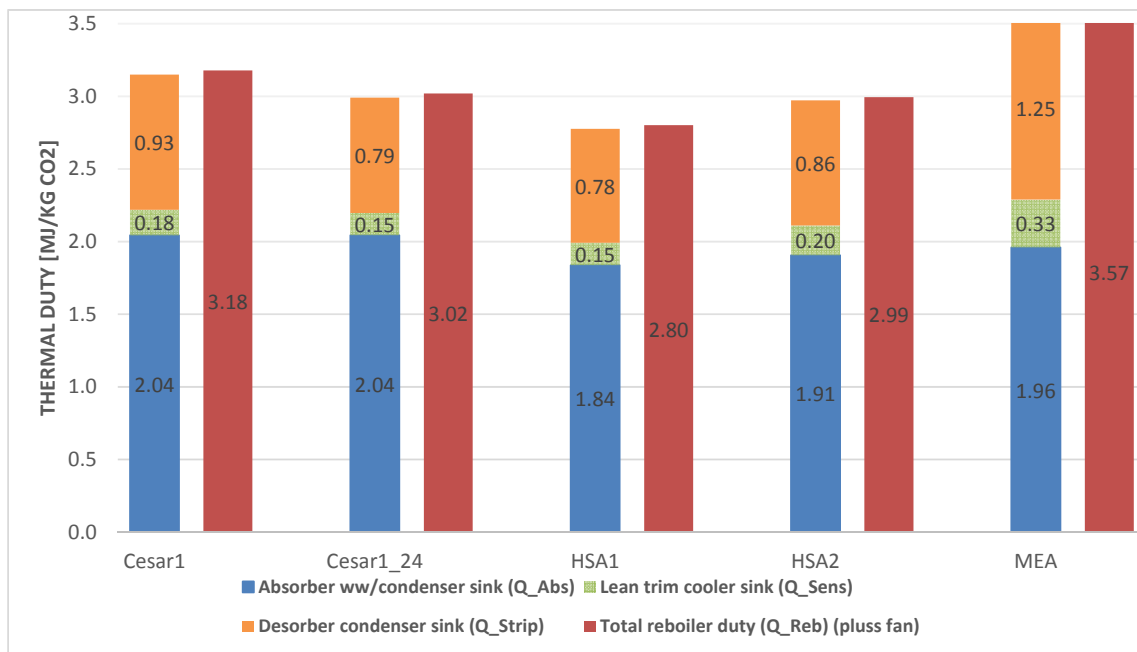Figure 4: Rigorously simulated heat sinks and sources for optimum cases (%)

Figure 5: Rigorously simulated heat sinks and sources for optimum cases (MJ/kg CO_2)

Table 3: Energy sink and source summary for HSA1, HSA2 and MEA

	MEA	HSA1	HSA2	%-reduction (HSA1)	%- reduction (HSA2)
Total reboiler duty (Q_Reb) (plus fan duty)*	3.57	2.80	2.97	22	17
Absorber WW/condenser sink (Q_Abs)	1.96	1.84	1.91	6	3
Desorber condenser sink (Q_Strip)	1.25	0.78	0.86	37	31
Lean trim cooler sink (Q_Sens)	0.33	0.15	0.20	53	38

*units in MJ/kg

5.2.2 The regeneration heat sinks: stripping steam and sensible heat

The overall efficiency increase for HSA1 compared to MEA is due to the reduced losses incurred in the regeneration section, Q_{Sens} (Eq. 13) and Q_{Strip} (Eq.14). The overall duty for HSA2 is slightly less energetically efficient than HSA1 (Table 3). The heat loss incurred in the absorber is larger for HSA2 (1.91 vs. 1.84 MJ/kg), and both the sensible heat- and the stripping steam requirements are larger (0.20 and 0.86 vs. 0.15 and 0.78 MJ/kg). The sensible heat requirement for HSA2, being directly proportional to the cyclic capacity, is slightly larger due to the larger circulation rate necessary for HSA2 to capture the same amount of CO_2 (see Figure 3). HSA1 requires a circulation rate that is about 20% higher than that for HSA1. Following this, the sensible heat requirement increases with 25%. As seen, although the increase is 25%, it only accounts for a minor portion of the overall SRD. It is also seen that the CO_2 stripping heat sink corresponds to the amount of steam leaving the desorber and therefore, see Table 4, the P_{H2O}/P_{CO2} ratio is slightly higher for HSA2.

As pointed out, the energy sinks are highly coupled and it is necessary to consider all sinks together when energetically evaluating new solvents. For example, for Cesar1, which has the highest regeneration efficiency, n_{eff} = 68%, the overall SRD is still larger than for HSA1 since the solvent heat of reaction is larger. Thus, as noted, the overall heat of absorption gives the thermodynamic limitation of the solvent. The effect of the stripping term vs temperature and the solvent heat of reaction, and their dependence on each other, is also shown by a simplified form of the Gibbs-Helmholtz equation, which predicts the effect of temperature on the vapour pressure ratio of water and CO_2 at the top of the stripper [20,40]:

$$\left(\frac{p_{H2O}^{sat}}{p_{CO_2}^*}\right)_{T=T_{Stripp}} = \left(\frac{p_{H2O}^{sat}}{p_{CO_2}^*}\right)_{T=T_{ref}} exp\left(\frac{\Delta h_{vap,H_2O}-\Delta h_{ABS,CO_2}}{R}\right)\left(\frac{1}{T_{ref}} - \frac{1}{T_{Stripp}}\right) \qquad (16)$$

Two important properties can be seen from this equation: The first is the *Temperature/pressure effect at constant heat of reaction.*
As long as the heat of reaction for the solvent is larger than the heat of vaporization of water, the vapor pressure ratio $\left(\frac{y_{H_2O}}{y_{CO_2}}\right)$ at the stripper top decreases with increased temperature/pressure.
In general, maximizing temperature swing will thus minimize vapor content at the stripper top and minimize the stripping term Q_{Strip} (Eq.14).
The second is the *Heat of reaction effect at constant pressure.* An increased absolute value of the heat of reaction (higher than the vaporization enthalpy of water) will increase the CO_2 partial pressure at a given total stripper pressure, thus lowering the required stripper temperature and steam stripping, thus lowering Q_{Strip}. Although the given equation gives insight to solvent trends, it does not include a detailed thermodynamic description of the solvent.

Comparing the solvents, as shown in Table 4, the maximum temperature swing is shown (ΔT_{stripp}) for the solvents. The highest temperature swing solvents at their optimums also show the highest regeneration efficiency. A larger temperature swing past the thermodynamic optimum, by further increasing duty, will drive the desorber sharply into a steam limitation regime, where excess steam is generated in the reboiler as stripping is limited by the solvent equilibrium relationship, as shown by

the first simulation runs in Figure 3.

5.3   The overall thermodynamic efficiency versus heat of reaction

In Table 4, the thermal regeneration efficiency value, n_{eff}, a measure of the thermodynamic reversibility of the process, is given with values of 55% for MEA and 66% for HSA1. If a hypothetical process was designed such that the energy to regenerate the solvent equals the heat of reaction, n_{eff} would equal unity, i.e, the process would need an input of an equal amount of energy as is released in the overall exothermic reaction in the absorber. It shows that the higher the value of n_{eff}, the more thermodynamically efficient the process is. Less heat is used for the sensible- and stripping steam sink and a larger percentage of the overall SRD is used for reversing the heat of reaction sink. This thus means that the solvent heat of reaction forms the limiting energy required, and should itself be minimized to the extent possible by the counteracting heat of stripping steam sink, with basis of sufficient absorption kinetics and phase equilibrium.

Table 4: Key results for the solvents

Optimum run		Cesar1 16.5m	Cesar1 24m	HSA1 24m	HSA2 24m	MEA 16.5m
n_{eff} [-]	[%]	63.8 %	67.7 %	65.6 %	63.6 %	54.8 %
Cyclic capacity	[g CO2/kg solvent]	98.9	118.6	113.1	85.6	59.9
P_{H2O}/P_{CO2} (top desorber)	[]	0.82	0.71	0.68	0.74	1.11
P_{H2O}/P_{CO2} (bottom desorber)	[]	29.48	54.85	56.10	89.76	13.70
ΔT_{stripp}	[°C]	23.3	26.93	26.7	25.5	18.0
SRD	[MJ/kg CO$_2$]	3.14	2.96	2.75	2.94	3.52
Steam loss absorber vent (Q_{abs})	[MJ/kg CO$_2$]	2.04	2.04	1.84	1.91	1.96
Regeneration steam (Q_{strip})	[MJ/kg CO$_2$]	0.93	0.79	0.78	0.86	1.25
Lean solution cooling duty (Q_{sense}) CO$_2$]	[MJ/kg CO$_2$]	0.18	0.15	0.15	0.20	0.33
Sum cooling	[MJ/kg CO$_2$]	3.15	2.99	2.78	2.97	3.54
SRD improvement compared to MEA (%)	[%]	11	16	22	16	-
P_{H2O}/P_{CO2} (top absorber)	[]	22.32	22.33	20.31	20.89	21.90

In Figure 6 is shown a plot of the stripping steam, Q_{Strip}, for each solvent at the optimum run versus the approximation as given by Eq. 14. The contribution to the thermal energy requirement [MJ/kg CO$_2$]is shown versus molar fraction of CO$_2$ at the top of the stripper column. It is for the Q_{Strip} approximation curve assumed that the rest of the stripping vapor is steam.
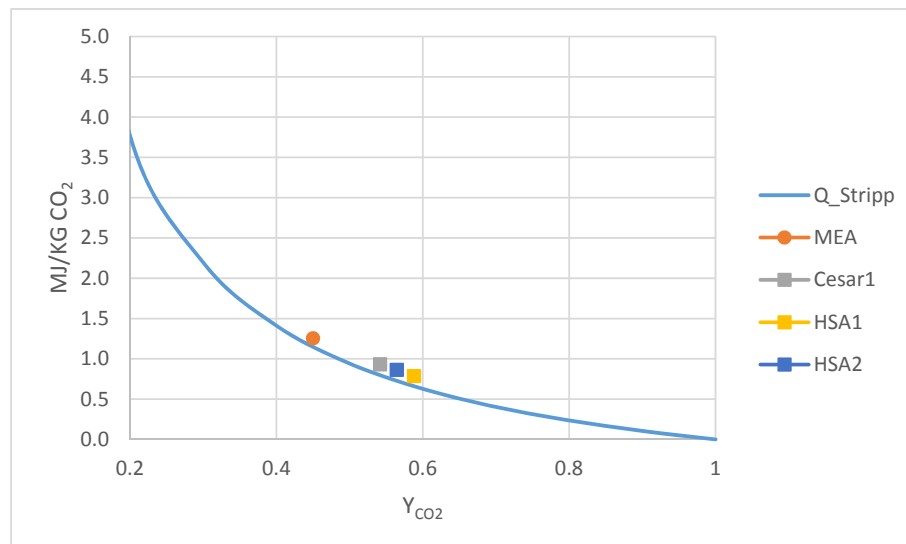
Figure 6: Approximated stripping steam (Q_{strip}) by eq. 14 as function of mole fraction CO_2 in stripper overhead. Real Q_{strip} for the solvents added for comparison.

The specific stripping steam requirement for MEA is 1.25 MJ/kg whereas that for HSA1 is reduced to 0.78 MJ/kg, a 37% reduction. As seen from the figure, it is possible to reduce this steam requirement further, but its effect on SRD requires increasingly higher CO_2 content at the desorber outlet (lower vapor diluent). Fine-tuned intra-process heat integration is necessary in order to reduce this further.

It is similar for the lean solution cooling duty. Figure 7 shows simulated values of Q_{Sens} versus the estimated values from Q_{Sens} (Eq. 13) for three different heat exchangers approach temperatures (5, 10, 15K). As shown in Eq. 13 , Q_{Sens}, reduction requires primarily lower circulation rate (L/G ratio) and/or an improved heat approach over the heat exchanger. Minimizing this value may party also be a process limitation and not just a solvent limitation, as there is a limit to the size of a heat exchanger. A too low circulation rate may affect wetting and other hydraulic phenomena in the columns and reboiler, which is especially important. As shown, for the optimized HSA1, with this energy sink accounting for only 6% percent of the overall SRD, any improvement will only marginally improve SRD.
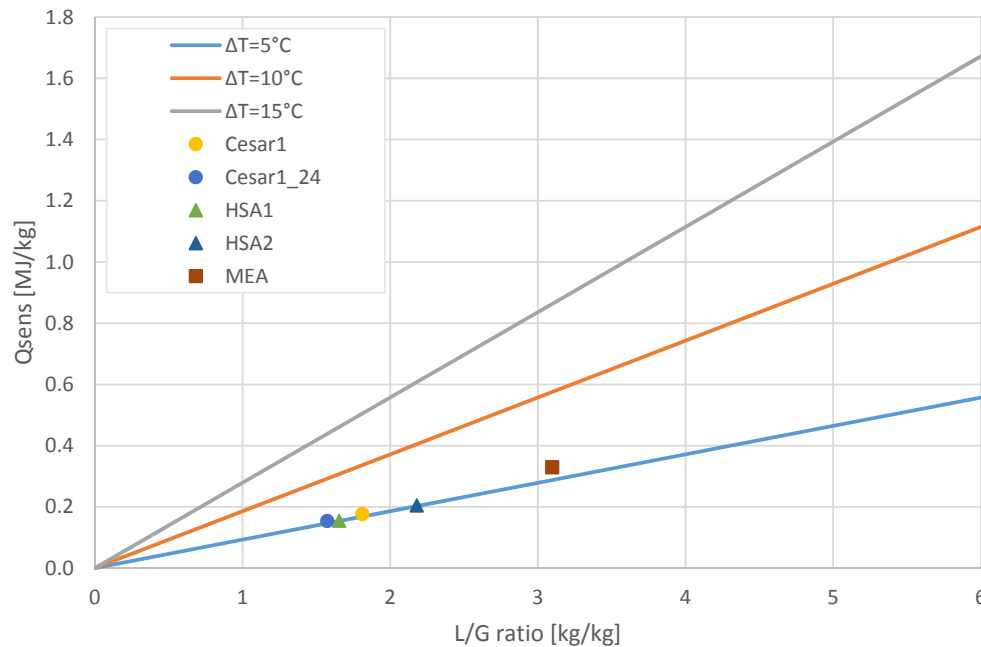

Figure 7: Approximated sensible heat (Q_{sens}) versus L/G ratio by Eq. 13 compared to actual for the various solvents. Shown are three different heat exchanger lean side temperature approaches. C_{pl} is 3.5 kJ/kg/K in the approximation.

5.4   Energy sinks combined for a standard process configuration

Reduction of both Q_{Strip} and Q_{Sens} will be increasingly more difficult, the more *optimized* the solvent is for the given flue gas purpose, however, process improvements may account for further energy savings. In Figure 8, a trend line is drawn showing the improved overall SRD for the different solvents, using a *standard process configuration*. For the given process, the circulation rate is proportional to SRD and it will become increasingly difficult to improve the process, the closer one reaches the thermodynamic limitation given by the solvent heat of reaction. In the figure, an L/G limitation is also

highlighted, which is assumed the case with a solvent of pure MEA, which is purely hypothetical, but gives the limiting liquid rate based on Eqn. 13. Higher heat of reaction may be favourable as long as the stripping and sensible heat terms are minimized, however, the absolute minimum SRD will then increase as shown in Figure 8, which is as noted based on the generic flow sheet depicted in Figure 1. Increased heat utilization by improved configurational design will potentially reduce stripping steam usage. The trend line is therefore dependent on the process configuration, and will change with improved internal heat utilization.
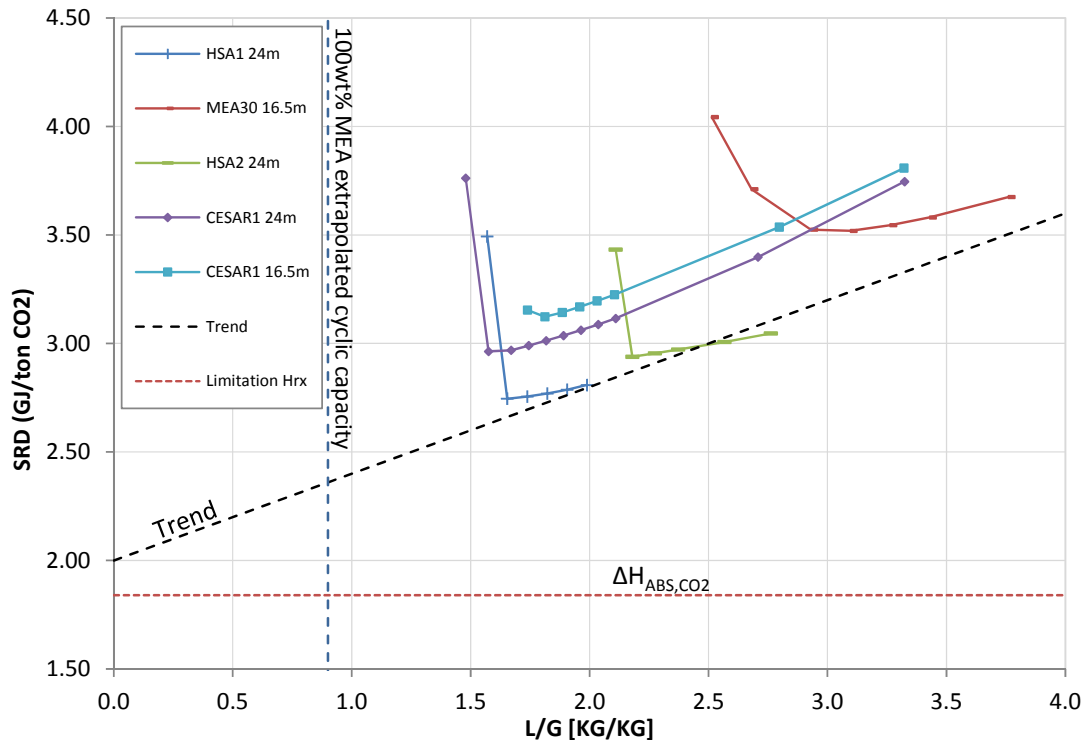
Figure 8: Minimum thermal reboiler duty for each solvent versus L/G. Theoretical minimum for a solvent with CO_2 absorption enthalpy of 85 kJ/mol shown as red line " $\Delta H_{ABS,CO2}$". Trend line shows expected pathway towards the potential of further energy savings considering the given process setup.

5.5   Potential for process improvement

Figure 9 shows the desorber partial pressure and equilibrium curve for the optimum case for HSA1. It is shown that a pinch condition is reached some meters below the top of the desorber column, indicated by a cross-over about 2 meters from the top. Above here, the driving force is for absorption. As discussed above and as shown with Eqs. 14 and 16, any flashing prior to the stripper inlet will lower the potential of reducing Q_{Strip}. Therefore, the solvent should be fed at its bubble-point temperature to maximize driving force and temperature swing efficiency of the stripper. This is a question of process design, and suggest that, based on the operating line in the figure, and the realization that this is the optimum run for the given configuration, that there is a modest potential for improvement of the configuration of the desorber and connected unit operations. This is a general issue for the generic process configuration discussed in this paper. Limiting flashing at the inlet, requires lower solvent rich temperatures, and will cause sub-optimal heat transfer in the cross flow heat exchanger for the generic process. Thus, a reduction in the stripping sink will therefore only increase the sensible heat sink, to

no overall improvement in SRD. Energy saving schemes must be designed such that the cross flow heat transfer is still as thermodynamically efficient as prior to the stripper modification.
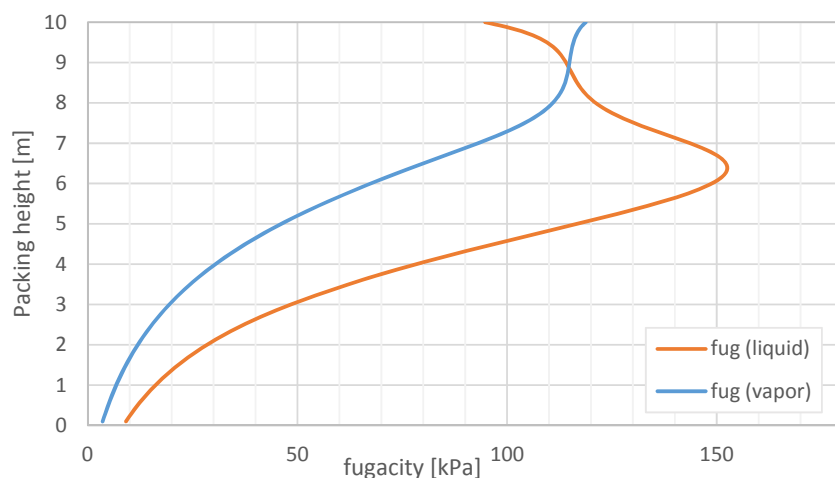

Figure 9: Equilibrium and operation lines along the stripper column for the best performing operation using solvent HSA1.

5.6 Possible ways of recovering losses incurred in the absorber

As can be seen from this analysis, in a thermal swing absorption process, the heat associated with the absorption of CO_2 is irreversibly lost in the process, and may not be re-used in reversing the reaction, given the process design. The solvent must therefore be optimized based on the initial flue gas CO_2 concentration. The remaining areas for improvement are the stripping steam requirement and the sensible heat requirement, in which both can potentially be reduced, by improved process design and by maximizing process reversibility. In a follow-up paper, improved process configurations are addressed that quantitatively determines, based on simulations using the solvents investigated in this work, what can be gained in overall energy reductions.

5.7 Specific power plant energy penalty for avoided CO_2

In the prior evaluations, the overall heat duty for separation is used for measuring the efficiency of the solvents under investigation. In the following discussion, the overall energy penalty for avoided CO_2 is estimated for the new solvents, to give a broader picture of the solvent performance. This overall capture cost, resulting in a parasitic load for the power plant, includes both capture and compression of CO_2 from the exhaust gas source, and can be divided into three parts. First part is steam extracted to the capture plant will give a loss of work or power output from the power plant. In this study this loss is estimated by assuming 75% adiabatic efficiency of an ideal Carnot thermal engine. This is a value commonly used in literature for example in [23]. The hot temperature is set 10°C higher than the reboiler temperature for sufficient driving force in the reboiler, while the cold temperature was set to 30°C, similar to the condenser cooling temperature. The resulting efficiency's and results are tabulated in table 5. The second part is the auxiliary CO_2 capture plant load which includes work for fans, solvent pumps, water wash and DCC pumps. This is labelled as W_aux in table 5, and is relative constant due to the fan work. The last part is the work for compression (W_Compression) of the CO_2. This work was calculated in Aspen Plus (GERG2008 EOS) with an integral compressor (80%, adiabatic efficiency) with 3 intercoolers (40C and a 2% pressure drop) compressing the CO_2 from ~2 bar to 110bar.

The total work lost (W_Tot) due to the cost of CO_2 capture and compression is shown in Figure 10. The solvent HSA1 has a net parasitic load of 0.27 kWh_{el}/kg CO_2. This is a 13% improvement relative to the MEA base case in table 5. The compression cost itself (2bar to 110bar for the given train), is 0.10 kWh_{el}/kg CO_2, or one third of the overall parasitic load relative to MEA.

To see the effect of increased thermal efficiency on overall power plant energy efficiency, it is of interest to see the results assuming the MEA base case with a 100% thermally efficient stripper (n_{eff} = 100%, Q_reb = 2.0 MJ/kg). This hypothetical case reduces W_reb to 0.10 kWh_{el}/kg CO_2 which then gives a net parasitic load of 0.23 kWh_{el}/kg CO_2, which is a 27% improvement from the real and current optimized MEA base case. Further optimization of the process flow sheet to reduce Q_Reb beyond this level is difficult, hence major improvements in reduction of lost work relative to solvent HSA1 (0.27 kWh_{el}/kg CO_2) is difficult to achieve. It can be concluded that the HSA1 solvent is highly optimised for CO2 capture from process flue gases at ambient pressure, with some further potential for stripping steam reduction based on further process optimization.

Table 5: Lost work analysis

|	MEA	Cesar1	HSA1	HSA2
Q_Reb [MJ/kg CO_2]	3.52	3.12	2.75	2.94
Reboiler Temp [C]	122.36	123.81	125.01	125.73
Thermal/adiabatic efficiency [%]	75.0 %	75.0 %	75.0 %	75.0 %
Ideal Carnot Efficiency [%]	25.2 %	25.5 %	25.7 %	25.9 %
Net thermal to electric efficiency [%]	18.9 %	19.1 %	19.3 %	19.4 %
W_Reb [kWh_{el}/kg CO_2]	0.185	0.166	0.147	0.158
W_aux [kWh_{el}/kg CO_2]	0.030	0.025	0.026	0.027
W_Compression [kWh_{el}/kg CO_2]	0.099	0.099	0.099	0.099
W_Tot (SEPAC) [kWh_{el}/kg CO_2]	0.314	0.291	0.272	0.284
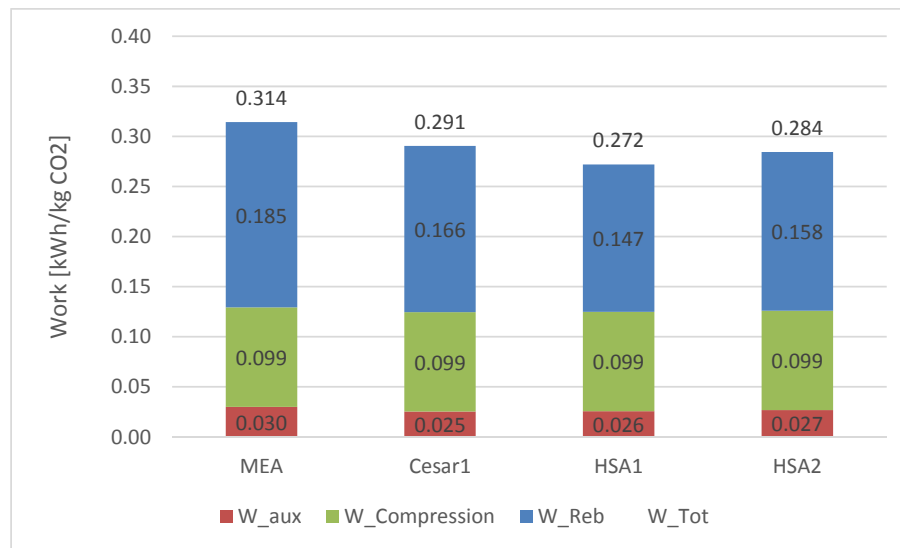
Figure 10: Work lost due to CO_2 Capture and compression to 110 bar

6. Conclusions

This work focuses on understanding the major energy losses incurred in an absorption/desorption process. An evaluation framework has been developed where energy sinks are coupled to process energy balances based on the basic principles of a thermal heat engine. This framework is used to directly quantify where heat is spent in the process. A comparison is made with three state-of-the-art solvents, where two are newly developed and undergoing current investigation, which then are benchmarked against MEA. It is shown with examples that the majority of the energy spent in an optimized absorption processes stems from compensation of the heat evolved in the absorber during chemical absorption. For a reversible process, the solvent heat of reaction at the absorber conditions will always form the theoretical minimum of heat required for regeneration. A result of this fact is that, firstly, an absorption/desorption process has its thermodynamic limitation equalling the absorption heat released in the absorber, giving the overall thermodynamic limitation of the solvent. Secondly, a higher solvent heat of reaction will in general lower the minimum stripping steam requirement for solvent regeneration, thus, in an aqueous solution an optimum will exist that minimizes both heat sinks. Higher regeneration temperatures and thus increased temperature swing will also reduce the stripping steam requirement, however, at the cost of higher value steam (increased Carnot heat-to-work engine efficiency) and increased reboiler duty. In the process of finding the best solvent, the heat of reaction should therefore be minimized to the extent allowable for adequate selectivity.

Investigation of the solvents are performed using the framework for heat duty analysis. An established base case has been used that represents a large scale application, with no particular process heat integration schemes. It is shown that the solvent *HSA1* is the best performing solvent based on the given process setup. The regenerative efficiency parameter for *HSA1* is 66% with an optimum specific reboiler duty (SRD) of 2.78 MJ/kg CO_2 removed, for a coal case based on a traditional process setup. This is a 22% reduction based on optimized MEA 30_{wt}%. This results in a specific power plant energy penalty for avoided CO_2 (SEPAC) of 0.27 kWh_{el}/kg CO_2.

It is shown that the investigated solvents show a high thermodynamic efficiency for coal fired flue gas CO_2 capture. The HiperCap solvents, HSA1 and HSA2 seem to be sufficiently fast to be used in an industrial absorber, although more work should be completed in order to establish accurate kinetics for the systems. There is room for further improvement by enhancing process reversibility by process configurational enhancements, which will reduce the stripping steam- and sensible heat requirements. As the HSA1 solvent already has efficient utilization of stripping steam, it is still expected that this value can significantly increase above the current value of 66%. A follow-up paper will address this potential.

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