



13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18
November 2016, Lausanne, Switzerland

Simulation and energy evaluation of two novel solvents developed in the EU project HiPerCap

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Abstract

Simulation results on minimum specific reboiler duty (SRD) are presented for two absorption solvent systems selected in the HiPerCap project, here referred to as HC#1 and HC#2. An established base case has been used that represents a large scale application, where heat loss can be neglected. Parameter optimization is performed to estimate the energetic potential of these solvents. In particular, full closed loop sheet simulations are run to find optimum operations with respect to specific reboiler duty at 90% CO₂ capture. These simulations have been performed with the motivation of understanding the energetic potential for post combustion CO₂ capture from a coal source. The HC#1 and HC#2 solvents are substantially more efficient than MEA, based in thermodynamic efficiency, both in terms of thermal heat requirement (SRD) and solvent circulation rate, and will improve operational costs. The SRD found for HiPerCap solvent 1 (HC#1) with the given defined base case was found to be 2.74 MJ/kg. The SRD was 2.94 MJ/kg for HiPerCap solvent 2 (HC#2) with the given defined base case was found to be 2.74 MJ/kg. In comparison, the SRD for MEA 30%wt was 3.61 MJ/kg. Both solvents are, based on the given assumption regarding kinetics, well suited for post combustion CO₂ capture.

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Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: CO₂ capture, process modelling, solvent development, process optimization

1. Introduction

The objective of this work has been to implement and perform detailed simulations of two novel solvents selected in the HiperCap project, here referred to as HC#1 and HC#2, to estimate the energetic potential of these solvents. In

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particular, full closed loop sheet simulations have been run to find optimum operations with respect to specific reboiler duty at 90% CO₂ capture. The resulting specific reboiler duty (SRD) is determined by varying the solvent circulation rate over a range of operating conditions, until a minimum is found. Other process units were set such as column heights, whereas the heat exchanger is always defined based on a temperature approach. This simulation analysis does not focus on other solvent properties such as degradation and emissions. Optimization is performed using the optimization utility functions in CO2SIM. 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 CO₂ flue gas removal. Thus, optimum loading ranges and circulation rates can be found by defining the capture degree, which in these simulations is set to 90% CO₂ removal from the exhaust gas.

1.1. Reference capture plant

In Figure 1 is shown a simplified flow diagram of the base case plant as simulated in CO2SIM. It has a conventional process structure. The base case includes a direct contact cooler (DCC), a flue gas fan and a water wash that recycles the condensed water back to the rich stream.

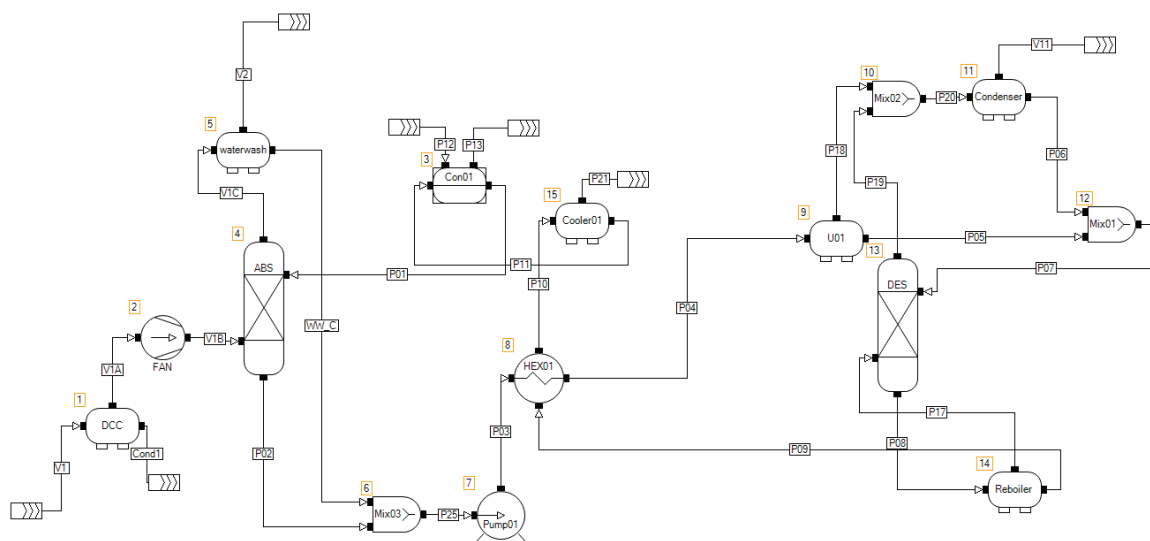


Figure 1: The reference plant configuration used in the study

1.2. Specific plant configurations and assumptions

The following assumptions apply for the base case:

- The simulations do not include the compression train
- HC#1 solvent has an amine concentration of 55 % mass in an aqueous solution
- HC#2 solvent has an amine concentration of 55 % mass in an aqueous solution
- All simulations have a specified removal rate of 90% (mol) CO₂ from the inlet flue gas
- The inlet flue gas comes from the HiPerCap project default coal power plant case (ASC) and is shown in Table 1.
- The heat exchangers are defined on a heat approach defined on the cold side (unless otherwise stated), to 5°C.
- The diameter was set so that the column never surpassed 70% of the velocity of flooding
- Desorber overhead pressure set to 2 bar

The base case process setup as well as unit sizes have been determined from a standardized base case as defined in the HiPerCap project. It resembles a full scale CO₂ capture plant from a coal fired plant [1].

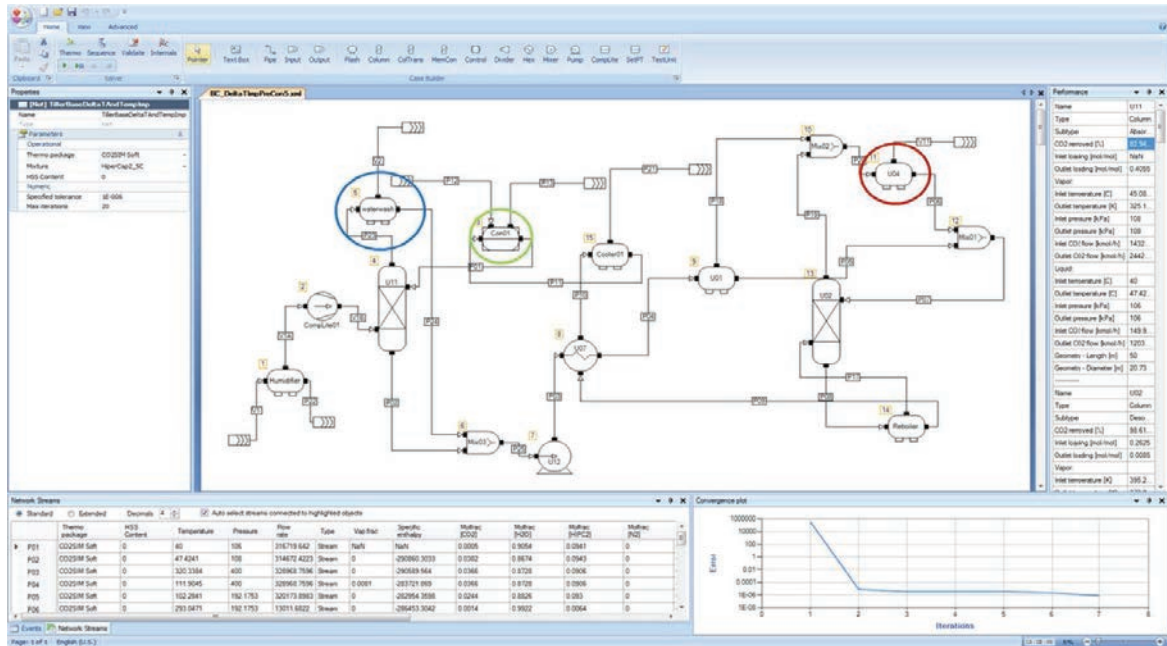


Figure 2: Flowsheet and visual representation of the CO2SIM software. Circles depicting the areas where the major heat sinks are.

1.3. Implementations of HC#1 and HC#2 Solvents

The developed model is based on experimental data and correlations from separate experiments in own laboratories, e.g. chemical equilibria, heat of reaction measurements, viscosity and density measurements. The main data used in describing the solvents are given in Hartono et al. [2]. Implementation practices and models are described in more detail in Tobiesen et al. [3,4]. Key focus was spent on thoroughly testing the novel solvents against a MEA base case. 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. [2]. All other necessary models, such as other physical property models and packing correlations based on earlier work, or if not available, approximated based on literature data. Detailed description of the model implementation and assumptions of the "soft-model" approach in CO2SIM is not given in further detail here, but can be obtained by contacting the authors.

1.4. Solvent kinetics for HC#1 and HC#2

The emphasis of this work has been to develop procedures for rapid understanding of a solvents potential for post-combustion CO₂ capture. Therefore, priority has been placed on obtaining VLE data before detailed kinetic data. These systems are both promoted with an activator to enhance the kinetics, and screening measurements show that the systems have sufficient kinetics to allow for a normal sized absorber for CO₂ capture from a coal fired power plant. However, as limited kinetic data are available at this point for the solvent systems, the measured height of the absorber is based on the assumption that the degree of equilibrium in the absorber bottom does not surpass 90-92% based on

the CO₂ loading level. These values should typically be possible in an industrial absorber and it is, based on screening measurements, assumed attainable for the two activated solvents.

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

Flue gas (kg/s)	801.09
Flue gas (kmol/h)	98 017
Flue gas Temp. [C]	47
Flue gas Press [kPa]	105
CO ₂ at inlet (mol % wet)	13.6 %
H ₂ O at inlet (mol % wet)	10.6 %

1.5. Optimum plant operation for the HC#1 solvent

By varying circulation rate and by keeping the CO₂ removal at a constant of 90%, an optimum point is found with respect to specific reboiler duty (SRD) for the flow sheet simulation. With the given base configuration, solvent circulation rate was perturbed about $\pm 20\%$ around the optimum with respect to the given criteria, shown as 7 separate points of operation. The specific reboiler duty (SRD) is shown versus circulation rate in Figure 3, and the results are also tabulated in Table 2 for the given points.

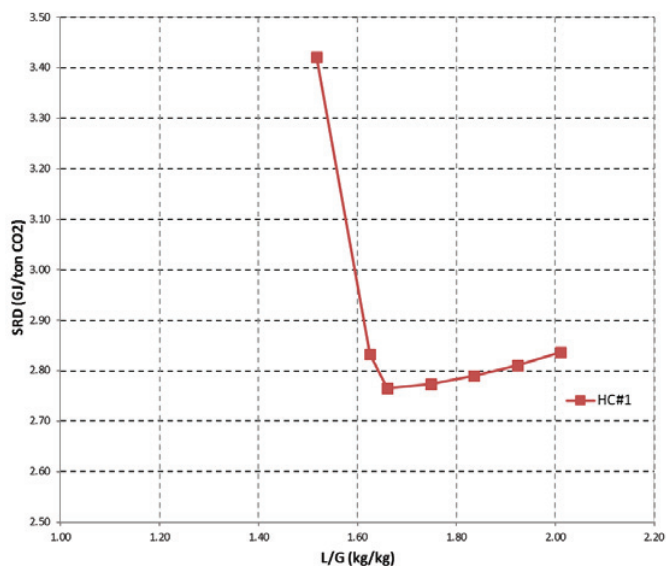


Figure 3: HC#1 solvent circulation rate versus SRD

Table 2: Summary data for HC#1 solvent

	Run1	Run2	Run3	Run4	Run5	Run6	Opt MEA
Absorber Data							
Solvent Lean flow rate (kmol/hr)	164392	157542	150692	143843	136993	130143	396800
Solvent Lean flow rate (kg/s)	1580	1513	1447	1380	1314	1247	2400
Solvent Lean Temp. [°C] into abs	40	40	40	40	40	40	40
Solvent Rich Temp. out of abs[°C]	47	46	46	46	46	46	48
Solvent Lean CO ₂ loading	0.09	0.08	0.07	0.05	0.03	0.01	0.20
Solvent Rich CO ₂ loading	0.60	0.61	0.62	0.63	0.64	0.65	0.48
Flue gas (kNm ³ /h)	2204	2204	2204	2204	2204	2204	2204
Flue gas (km ³ /h)	2485	2485	2485	2485	2485	2485	2485
Flue gas Temp. [°C]	47	47	47	47	47	47	47
Flue gas Press [kPa]	105	105	105	105	105	105	105
CO ₂ at inlet (mol %wet)	13.6	13.6	13.6	13.6	13.6	13.6	13.6
H ₂ O at inlet (mol %wet)	10.2	10.2	10.2	10.2	10.2	10.2	10.2
CO ₂ recovery (%)	90 %	90 %	90 %	90 %	90 %	90 %	90 %
CO ₂ Captured (kg/s)	146.6	146.6	146.6	146.6	146.6	146.6	146.6
Stripper Data							
Reboiler Pressure [kPa]	205	205	205	205	205	205	205
Reboiler Temperature [°C]	123	123	124	124	125	125	122
Condenser Temperature [°C]	30	30	30	30	30	30	30

Reboiler Duty [MW]	412	409	406	404	403	508	935
Specific Reboiler duty [GJ/ton CO ₂]	2.81	2.79	2.77	2.76	2.74	3.46	3.61
Specific solvent requirement [kg Amine/kg CO ₂ removed]	10.77	10.32	9.87	9.41	8.96	8.50	17.52
Hex rich temperature in (°C)	47	46	46	46	46	46	48
Hex rich temperature out (°C)	113	113	113	113	112	112	116
Hex lean temperature in (°C)	123	123	124	124	125	125	122
Hex rich temperature out (°C)	52	51	51	51	51	51	53
Hex cold pinch (°C)	5	5	5	5	5	5	5
Hex hot pinch (°C)	10	10	11	12	13	13	6
Liquid/Gas ratio[kg/kg]	1.99	1.91	1.82	1.74	1.65	1.57	3.23

As can be seen from Table 2, the optimum simulation shows an SRD of 2.74 GJ/ton CO₂ with a circulation rate of 1314 kg solvent/s or a L/G ratio of 1.65. In the absorber, the degree to equilibrium based on loading level reaches 90% and based on CO₂ partial pressures, a degree of 55% at the bottom of the absorber. The lean loading level for the optimum is low, 0.03 mol/mol, which indicates that the solvent, based on a thermodynamic evaluation, is easily regenerated and produces a large CO₂/H₂O ratio at the top of the stripper column. The rich loading level is 0.64, yielding a cyclic capacity of more than 0.6 mole CO₂ pr mole amine.

1.6. Energy analysis HC#1 Solvent

For the case with lowest SRD, Run5 in Table 2, total reboiler duty is 402MW. Of this, the energy loss by steam lost at the absorber vent is 60%, while 28% of the heat is lost in the regeneration section (steam lost into the condenser), and 12% percent is lost at the lean cooler unit, with a reference temperature of 40°C (defined as the DCC cooling temperature). In the lean-rich cross heat-exchanger, 350MW is transferred from the lean to the rich stream as internal heat transfer. The heat exchanger size is such that the assumed approach on the cold side is 5°C.

1.7. Comparison to 30% mass MEA

In Figure 4, Table 3 and Table 4 are shown comparative plots or results with 30% mass MEA. HC#1 solvent has a significantly lower SRD, compared to the optimum MEA case. Another interesting note is the significantly reduced solvent circulation rate requirement, which is almost halved. This is a measure of the amount of solvent needed on a mass basis, i.e., a cyclic capacity, and shows that this system can be operated with half the mass circulation rate, compared to MEA. Thus, electric work for circulation of the solvent between absorber and desorber should also be halved

In Table 4, the major heat sinks are shown, based on a steam and heat analysis across the flow sheet. Not surprisingly, the largest heat sink is found in the absorber, where the main source is the heat of reaction for CO₂ absorption. The resulting exothermic heat that evolves during the absorption causes solvent heating, but mostly evaporation. There are two main options or pathways to eject the absorption heat generated inside the absorber column. Either as latent heat by

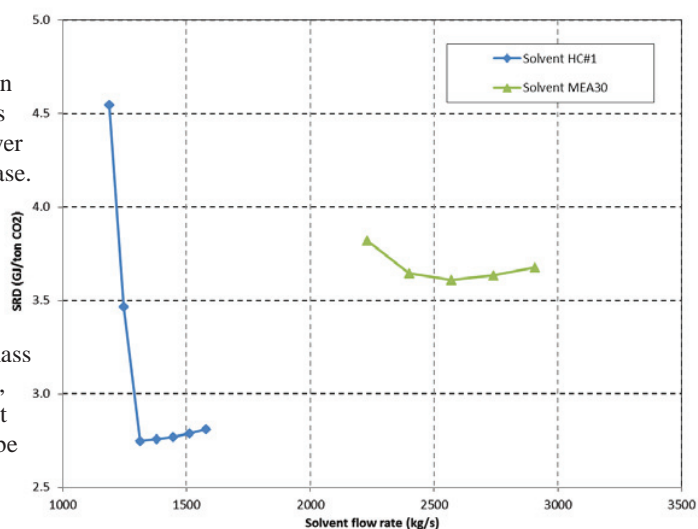


Figure 4: SRD vs. solvent flow rate for HC#1 and 30%MEA at 90% overall capture

evaporation of water into the absorber gas exit or as sensible heat in the rich solvent leaving the absorber sump. In post-combustion absorption processes, a significant portion of the absorption heat is ejected from the column by water evaporation in the absorber gas vent. This can readily be observed by the small temperature difference between absorber rich and lean solvent streams, henceforth most absorption heat must be ejected into the absorber gas vent. Thus the absorber water-wash section must also function as a condenser, and this absorber condenser duty is actually significant larger, than the desorber condenser duty. Additionally, it is this absorber condenser duty that generates the driving force for re-capturing of the lost amines that are captured in the absorber water wash. Circulation of water alone without cooling in the absorber water-wash would only result into a saturated state of the wash-water subsequently resulting in a state of equilibrium with no capturing of the lost amines in the effluent gas. The steam or water vapor leaving the absorber section vent is, if not used in any other way, lost and there is usually no means of recovering this heat i.e it is transferred irreversible into the cooling water. The more water vapor that leaves here, the larger cooling demand is required in the overhead absorber water-wash sections. Comparing HC#1 with MEA, this heat sink increases for HC#1, with values of 208MW and 246MW, respectively. This is common for aqueous solvents with larger CO₂ cyclic capacity, as the circulating solvent flow rate is lower, increasing evaporation and thus vapor losses out of the absorber section. Approximately 290 MW heat is generated inside the absorber column by assuming an absorption heat of 2.0 MJ/kg CO₂, hence approximately ~90% of the absorption heat for solvent HC#1 is ejected into the absorber water-wash section. This constitutes of almost 60% of the total SRD or heat input for HC#1. This happens even when the absorption heats of reaction have similar or even slightly lower values than that for MEA. However, looking at the regeneration steam requirement and the lean solution cooling duty, they are both reduced with 37% and 59% respectively, compared to MEA.

Table 3: Summary comparison of HC#1, HC#2 and MEA

Solvent Companion	Opt HC#1	Opt HC#2	Opt MEA
Solvent Lean flow rate (kg/s)	1314	1731	2569
Solvent Lean Temp. [°C]	40	40	40
Solvent Rich Temp. [°C]	112	113	116
Solvent Lean CO ₂ loading	0.04	0.02	0.20
Solvent Rich CO ₂ loading	0.64	0.42	0.48
Max. Theo. Loading % (abs. bottom)	92	91	91
Flue gas (kNm ³ /h)	2204	2204	2204
Reboiler Duty [MW]	403	431	530
CO ₂ recovery (%)	90 %	90 %	90 %
Specific Reboiler duty [GJ/tonn CO ₂]	2.74	2.94	3.61
Specific solvent requirement [kg Amine/kg removed]	8.96	11.82	17.52

Table 4: Energy sink analysis of HC#1, HC#2 and MEA

	MEA OPT	HC#1_OPT	HC#2_OPT	%-change (HC#1)	%-change (HC#2)
Total reboiler duty (MW _{TH})	-538	-411	-439	76	82
Absorber WW* cooling duty (MW _{TH})	208	246	239	118	115
Desorber cooling duty (MW _{TH})	196	115	126	59	64
Lean cooling duty (MW _{TH})	134	50	74	37	55

*Water-Wash

1.8. Optimum operation of the HC#2 Solvent for the base case configuration

In the comparison of HC#2, the exact identical flow sheet was used in CO₂SIM as with HC#1. The solvent models were changed and the concentration adjusted. Table 5 shows results at different circulation rates with the set base case configuration at a 90% capture rate. The best performing run with respect to reboiler duty is Run 7, giving an SRD of 2.94 GJ/ton, with a solvent circulation rate of 1731 kg/s yielding an L/G ratio of 2.18 kg/kg (see Table 5). The absorber reaches a degree to equilibrium based on loading level of 91% at the bottom of the absorber, and based on CO₂ partial pressures 61% at the bottom of the absorber. According to this model implementation, it is possible to reach a lean

loading level at around 0.02 before reaching the steam break-through in the desorber column, and there is still driving force at the absorber top liquid entrance for 90% CO₂ capture for coal flue gas concentrations. The rich loading for this case is 0.42 giving a cyclic capacity of 0.40. The lean loading level for the optimum is thus very low for both solvents.

Table 5: Summary data for HC#2 solvent

	Run1	Run2	Run3	Run4	Run5	Run6	Run7	Run8
Absorber Data								
Solvent Lean flow rate (kmol/hr)	235059	226832	218605	210378	202151	193924	185924	175924
Solvent Lean flow rate (kg/s)	2194	2117	2040	1962	1885	1807	1731	1638
Solvent Lean Temp. into abs[°C]	40	40	40	40	40	40	40	40
Solvent Rich Temp. out of abs[°C]	49	49	48	48	48	48	47	47
Solvent Lean CO ₂ loading	0.06	0.06	0.05	0.05	0.04	0.03	0.02	0.01
Solvent Rich CO ₂ loading	0.38	0.39	0.39	0.40	0.40	0.41	0.42	0.42
Flue gas (kNm ³ /h)	2204	2204	2204	2204	2204	2204	2204	2204
Flue gas (km ³ /h)	2485	2485	2485	2485	2485	2485	2485	2485
Flue gas Temp. [C]	47	47	47	47	47	47	47	47
Flue gas Press [kPa]	105	105	105	105	105	105	105	105
CO ₂ at inlet (mol %wet)	13.6	13.6	13.6	13.6	13.6	13.6	13.6	13.6
H ₂ O at inlet (mol %wet)	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2
CO ₂ recovery (%)	90 %	90 %	90 %	90 %	90 %	90 %	90 %	88 %
CO ₂ Captured (kg/s)	146.6	146.6	146.6	146.6	146.6	146.6	146.6	146.6
Stripper Data								
Reboiler Pressure [kPa]	205	205	205	205	205	205	205	205
Reboiler Temperature [°C]	123	124	124	124	125	125	126	126
Condenser Temperature [°C]	30	30	30	30	30	30	30	30
Reboiler Duty [MW]	447	444	441	438	436	434	431	421
Specific Reboiler duty [GJ/ton CO ₂]	3.05	3.03	3.01	2.99	2.97	2.96	2.94	2.94
Specific solvent requirement [kg Amine/kg removed]	14.97	14.44	13.91	13.38	12.85	12.33	11.82	11.44
Hex rich temperature in (°C)	49	49	48	48	48	48	47	47
Hex rich temperature out (°C)	114	114	114	114	114	113	113	113
Hex lean temperature in (°C)	123	124	124	124	125	125	126	126
Hex rich temperature out (°C)	54	54	53	53	53	53	52	52
Hex cold pinch (°C)	5	5	5	5	5	5	5	5
Hex hot pinch (°C)	9	10	10	11	11	12	12	13
Liquid/Gas [ratio kg/kg]	2.76	2.67	2.57	2.47	2.37	2.28	2.18	2.06

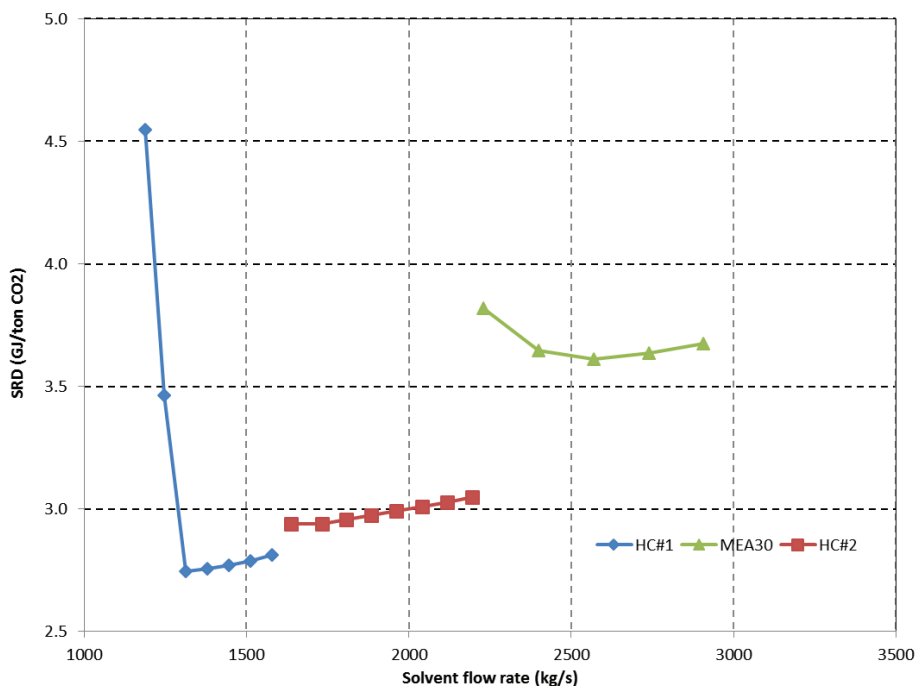


Figure 5: Solvent circulation rate versus SRD for HC#1, HC#2 and MEA.

Comparing HC#2 with the other solvents HC#1 and MEA it is seen that this solvent seems to be slightly less efficient than HC#1, for the given process. Figure 5 shows different plot of the optimum performing run. It is shown in Figure 5 that for HC#2, the optimum circulation is about 20% higher than for HC#1 whereas reboiler temperatures are similar, with a simulated optimum temperature of 125 °C and 126 for HC#1 and HC#2 respectively.

1.9. Summary and conclusions

These simulations have been performed with the motivation of understanding the energetic potential for post combustion CO₂ capture from a coal fired power plant source. Although the simulations are run with rate-based models, the kinetics have uncertainties. In general, the kinetics of HC#1 and HC#2 seems to be sufficiently fast to be used with an 24 meter absorber, although, more work should be done in order to determine specific kinetics for the system. Both these solvents has an activator amine which significantly increases the reaction kinetics, making both system capable of low partial pressure absorption, i.e. 90% absorption of coal flue gas sources.

The HC#1 and HC#2 solvents are substantially more efficient than MEA, based in thermodynamic efficiency, both in terms of thermal heat requirement (SRD) and solvent circulation rate, and will improve operational costs. A follow up paper which is currently underway will give a deeper analysis of the potential of the solvents as well as suggestions for improved process operations.

Specific findings:

- The SRD found for HiPerCap solvent 1 (HC#)1 with the given defined base case was found to be 2.74 MJ/kg.
- The SRD was 2.94 MJ/kg for HiPerCap solvent 2 (HC#2) with the given defined base case was found to be 2.74 MJ/kg. In comparison, the SRD for MEA 30%wt was 3.61 MJ/kg.

Both solvents are, based on the given assumption regarding kinetics, well suited for post combustion CO₂ capture.

Acknowledgements

This work was performed within the HiPerCap project. The project receives funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 608555. The industrial partners who also financially support the project are gratefully acknowledged.

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