Comparative studies of CO_2 capture solvents for gas-fired power plants: Integrated modelling and pilot plant assessments

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Abstract- Natural gas accounts for 21.3% of the total primary energy supply. In particular, with the shale gas boom, its application has experienced an exponential growth rate. Nevertheless, natural gas has the highest hydrogen to carbon ratio among all hydrocarbons and the dilute (with respect to CO_2) exhausts of its combustion pose considerable thermodynamic challenges for carbon capture. Solvent-based carbon capture can potentially mitigate the carbon emissions. Nonetheless, minimizing the penalties associated with the costs of carbon capture requires detailed understanding of the underlying physical and chemical phenomena. The present research exploits a rigorous methodology based on rate-based distributed modelling and statistical associating fluid theory (SAFT). The important characteristics of this modelling approach include abstract formulation in conjunction with high predictability. The present research aims at establishing the performance of a new solvent (an amine-promoted buffer salt, APBS) in comparison to the baseline solvent, *i.e.*, monoethanolamine (MEA). The features of interest include: (i) developing a high fidelity mathematical model of the carbon capture process, (ii) validating the model with pilot plant data, (iii) quantification of the energetic and technical performances of the solvents using key process indicators (KPIs), and (iv) employing optimization programming for further solvent performance improvement.

Keywords: Solvent-based carbon capture, SAFT, rate-based modelling, model validation, optimization, MEA, APBS, GCCmax.

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1. Introduction

Increasing energy demand and associated pollution have posed an important paradoxical challenge toward the security of energy supply and environmental protection. This has translated into various national and global policies and regulations. The instances of these international regulations include the so-called Europe 2020 which targets 20% reductions in greenhouse gases, 20% energy supply from renewables, and 20% improvement in energy efficiency. In the UK, the Climate Change Act 2008 mandates an 80% overall cut in six greenhouse gases by 2050 compared to the 1990 baseline. While integration of renewable energy resources can moderate the problem to some extent, the Intentional Energy Agency (IEA) asserts that in a foreseeable future, fossil fuels remain the dominant source of energy supply, and application of carbon capture technologies will become increasingly urgent (IEA 2014a).

Natural gas (NG) accounts for 21.3% of the global primary energy supply (IEA 2014b) and with the shale gas boom, its application has experienced an exponential growth rate. Nevertheless, natural gas has the highest hydrogen to carbon ratio among all hydrocarbons and the dilute (with respect to CO_2) exhausts of its combustion pose considerable thermodynamic challenges for carbon capture. Amongst various carbon capture methods, post-combustion has the advantage of being an end-of-pipe treatment, requiring a minimal of retrofit to the existing energy infrastructure. In particular, solvent-based carbon capture has been already applied in ammonia and natural gas sweetening processes and is deemed to be the most commercially viable technology for end-of-pipe waste treatment of power plants. Furthermore, solvent-based carbon capture has proved to be an efficient method for increasing the yield of biorefineries (Sharifzadeh, et al., 2015) and emission reduction in the iron and steel industry (Ho et al., 2013).

In the recent years, developing solvents with superior techno-economic performance has been the focus of academic and industrial researchers. Frimpong et al., (2013) compared the performance of a proprietary amine-carbonate blend for carbon capture from coal-derived flue gas. The comparison with MEA baseline solvent was made based on carbon capture efficiency, energy of solvent regeneration, and overall mass transfer rate. Both solvents were studied at similar experimental conditions. Moser et al., (2011a,b) evaluated the performance of a solvent developed by BASF in a highly instrumented pilot plant in Niederaussem. They used CHEMASIM, an in-house simulation software tool, for data reconciliation and model validation. Their results suggested a high correlation between the reboiler duty, the desorber pressure, solvent circulations

rate, and solvent heat of absorption. Similar observation was made by Bumb et al., (2014) who studied the performance of a novel solvent optimized for coal-fired flue gas, at TNO pilot plant, Netherlands. They studied variation of the desorber top pressure between 0.8-1 barg, while maintaining the reboiler temperature constant. They reported that reboiler heating duty and solvent circulation were both minimum at 0.8 barg. However any further reduction would result in unacceptable condensate rate from the desorber overhead. Mangalapally et al., (20111a,b, 2012) conducted pilot plant studies for four new solvents. They identified the solvent circulation rate as the most influential operating parameter for pilot plant operation. Rabensteiner et al., (2014) studied pilot scale performance of ethylenediamine (EDA) compared to MEA using literature data. Cousins et al., (2012, 2015) studied the performance of concentrated piperazine and MEA in an Australian pilot plant. They observed that at elevated liquid/gas ratio, absorber intercoolers can mitigate the regeneration energy requirements by 10%. They also reported that rich solvent split can result in less reboiler and condenser duties.

An ideal solvent should have high CO_2 loading, fast reaction kinetics, low vapour pressure, negligible corrosiveness, and high thermal stability, in addition to a lower cost. Often these criteria are interdependent and require establishing a compromise. Oexmann and Kather (2010) provided an analytic analysis of thermal requirements for solvent regeneration heating duty, as a function of (i) solvent sensible heat (energy needed to increase the solvent temperature from absorber temperature to desorber temperature), (2) heat of evaporation (to produced stripping steam in the desorber), and (3) heat of desorption (needed to break the solvent-CO_2 bound). They demonstrated that these solvent characteristics are often interdependent. Solvents with a high heat of absorption often feature a higher kinetic rate. Furthermore, since the desorber can be operated at a higher pressure and the reboiler can be operated as a higher temperature, the water reflux from the desorber overhead is lower; hence the heating duty of the desorber will be also lower. Furthermore, a faster kinetic enables higher CO_2 loading and therefore, resulting in less solvent circulation rate and hence less sensible heat requirement. Nevertheless, the maximum allowable temperature in the desorber depends of the solvent thermal stability against degradation reactions. By comparison solvents with a lower heat of absorption may benefit from operating the desorber in vacuum operating conditions, at the costs of a higher power requirement for CO_2 compression.

More recent studies have focused on solvents with additional functionalities. For example, ammonia is regarded as a cost-effective solvent for CO_2 separation. However, low absorption rates limit the practical

application of this solvent. Yang et al., (2014) investigated the effects of adding potassium sarcosinate as the rate promoter to the ammonia solvent. Similarly, Thee et al., (2012) showed that the addition of small quantities of MEA to potassium carbonate solvent results in radical increases in the overall reaction rate. Recently, a new class of solvent is introduced, which exploit phase change in order to limit the energetic penalties of solvent regeneration. For example as shown by Liebenthal et al., (2013), an amine blend can form two liquid phases under certain CO_2 loading conditions. Then, a large energy saving is possible by sending only the CO_2-rich phase to the desorber. Furthermore, Ionic liquids are a promising class of solvents for carbon capture. The tunability of the ionic liquids' structure and properties offers several advantages such as lower energy requirement for solvent regeneration, higher thermal stability, and lower vapour pressure. However, the high production cost of ionic liquids is a barrier that needs to be addressed for their commercialization, (Chen et al., 2014).

Finally, process optimization has been the focus of various studies. Lee et al., (2013) investigated the performance of several amine solvents. They demonstrated a strong trade-off between the capital investment and operating costs using Pareto front diagrams. Mores et al., (2012) studied simultaneous optimization of the dimensions of the process equipment and process operating conditions. Three scenarios were considered in which reboiler duty was being optimized with respect to different combinations of reboiler inlet liquid flow-rate, reboiler inlet solvent composition, reboiler pressure, CO_2 loading and CO_2 recovery target. They observed a correlation between the optimal solvent CO_2 loading and the CO_2 recovery targets. In addition, they reported that as CO_2 loading increases, the specific heating and cooling duties (per unit of CO2 recovered) decrease. Hopkinson et al., (2014) developed a simple method for optimization of a conceptual solvent based on properties of commercial amine solvents. Solvent heat of reaction was applied in order to estimate the sensible and stripping heat of the process. They reported the value of 71 kJ/mol CO2 for the heat of reaction and the value of 0.1034 kWh/kg CO2 for the total equivalent work in the case of 90% CO2 recovery from coal-fired flue gases. Damartzis et al., (2015) proposed a module-based generalized design framework in order to synthesize the optimal process flow diagram. Features of interest included the stream topologies, the heat redistribution and the cascades of desorption columns for several commercially available solvents. Significant economic improvement (15%-35%) and reductions in the reboiler duty (up to 55%) were observed. Recently, Burger et al., (2015) proposed a hierarchical methodology based on a group contribution method which considers the molecular decisions at the same level of process design decisions. They demonstrated their

method for selection of the optimal solvent over a wide range of ethers, for CO_2 separation from a methane-rich mixture.

Several common conclusions can be drawn from the aforementioned theoretical and pilot plant studies.

- In establishing the performance of new solvents, there is always a need for a well-understood and predictable reference solvent such as monoethanolamine (MEA) which facilitates pilot plant testing runs and provides benchmark performance measures.
- Due to interdependencies of process operating specifications and combinatorial characteristics of the involved parameters, the pilot plant studies were often conducted in conjunction with simulation and optimization software tools.
- The pilot plant operating conditions are solvent-specific and the performance of each solvent should be studied at its corresponding optimal specifications.
- There is a need for key performance indicators which are not solvent-specific and are reproducible for different solvents.

The present research aims at benchmarking the performance of a new solvent called GCCmax. The GCCmax solvent is a novel solvent recently developed by Carbon Clean Solutions Limited (CCSL) for carbon capture from natural gas combustion exhausts and belongs to the class of amine-promoted buffer salt (APBS) solvents. The conducted research is comprehensive and include, pilot plant studies, model development and validation, and optimization in order to provide guidelines for further solvent optimization. The novel contribution of the present research includes:

1. Developing high fidelity multi-scale models for post-combustion carbon capture and validating the model for the case of the GCCmax and MEA solvents using pilot plant data.
2. Quantification of the performance of the solvents using a novel set of key performance indicators (KPIs), that enables objective and reproducible comparisons.
3. Identification of further opportunities for process optimization in terms of equipment design, operating conditions, and solvent composition.

The rest of the manuscript is organized as follows. Firstly, the research methodology is discussed. The features of interest include the applied modelling approach and underlying assumptions. Then, the results of model validation are presented and compared for the baseline MEA solvent and the new GCCmax solvent. The

comparison is made based on several novel key process indicators which quantify the difficulty of separating CO_2 from the flue gas. These "technical" KPIs are used as substitutes for economic indicators because using the latter to compare alternative solvents would suffer from assumptions around the cost of capital, the capital estimation method and the cost of utilities, limiting the reproducibility of the results. The last part of the paper explores the opportunities for further improvement of the new solvent performance through optimization with respect to process equipment, operating conditions, and the solvent composition.

2. Methodology

The research methodology is based on a multi-scale process modelling and optimization. Firstly, a rigorous process model was developed based on accurate understanding of the involved physical and chemical phenomena and rate-based modelling of gas-liquid contactors. Then, the developed model is validated using pilot plant data. Finally, the validated model is optimized for various design and retrofit scenarios.

2.1. Process model development

The accurate modelling of the solvent-based CO_2 capture processes for the purposes of solvent benchmarking and comparison requires thorough understanding of the underlying physical and chemical phenomena involved in absorption and desorption of CO_2 into and from the working solvent. The methods for modelling gas-liquid contactors can be broadly classified into equilibrium and rate-based models. Early-stage attempts for modelling gas-liquid separation processes were based on the assumption that at each separation stage, the exiting phases are in equilibrium conditions. Such assumptions were also incorporated into graphical methods (McCabe et al., 2004). However, it was widely observed that for most industrial applications assuming equilibrium composition of the exiting phases results in unrealistic predictions. The first attempt to overcome this limitation was to consider an efficiency measure for each separation stage, (McCabe et al., 2004), which can be applied to calculate the actual number of stages from the theoretical number of stages. Application of empirical efficiency correlations has been promising for binary and close-boiling separation systems. However, it was widely observed that for multicomponent systems, the efficiency of separation stages can vary from 5% for absorption systems with high viscosity, high molecular weight solvents to 120% in single-liquid-pass large-diameter distillation trays (or packed segments) because of the crossflow effect (Seader et al., 2013). Due to difficulties associated with uncertainties in the stage efficiency method, intensive research was devoted to developing non-equilibrium models based on transport rates (Waggoner and Loud, 1977; Krishna and Standart

1979; Taylor and Krishna, 1993; Krishnamurthy and Taylor, 1985; Taylor et al., 1994). The rate-based models are founded on the two-film theory, as shown in Fig. 1. Here, thermodynamic equilibrium is assumed only at the interface of vapour and liquid phases. Unlike equilibrium-based models, the exiting vapour phase is superheated and the exiting liquid phase is subcooled and they have different temperatures. The exchanged mass and energy between phases depend on the driving forces, transport coefficients, and the interfacial area. Often, both convective and diffusive transport phenomena are involved and component-coupling effects should be considered (Seader et al., 2013). Various empirical correlations for calculating the mass transfer coefficient are proposed by researchers for random packing (Onda et al., 1968; Bravo and Fair, 1982) and structured packing (Bravo et al., 1985, 1992). Finally, the bulk liquid and gas phases may have different flow configurations such as plug or mixed flows.

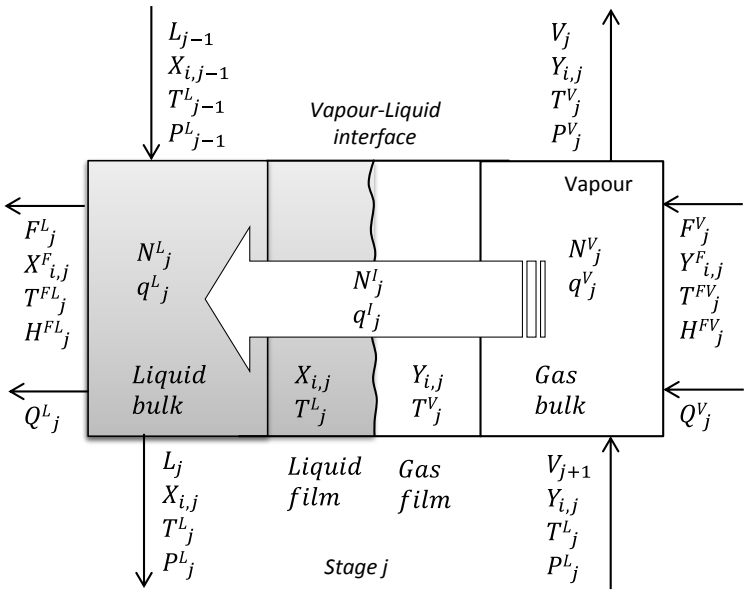


Fig. 1. Two-film model used for modelling rate-based absorption and desorption of CO_2 into and from solvent, (Zhang et al., 2009).

2.2. Reaction kinetics and thermodynamics

A full space rate-based representation of CO_2-solvent gas-liquid contactors requires detailed modelling of underlying chemical reactions, column hydraulics, as well as mass and heat transfer phenomena. For the case of CO_2 capture using alkanolamines, this would require modelling a series of speciation reactions as follows (Mac Dowell et al., 2010):

$$2H_2O \leftrightharpoons H_3O^+ + OH^- \quad (1)$$

$$CO_2 + H_2O \leftrightharpoons HCO_3^- + H^+ \quad (2)$$

$$CO_2 + OH^- \leftrightharpoons HCO_3^- \quad (3)$$

$$CO_2 + RNH_2 \leftrightharpoons RNH_2^+CO_2^- \quad (4)$$

$$RNH_2^+CO_2^- + RNH_2 \leftrightharpoons RNHCO_2^- + RNH_3^+ \quad (5)$$

$$RNHCO_2^- + H_2O \leftrightharpoons RNH_2 + HCO_3^- \quad (6)$$

where for the case of MEA, R=HO-CH2-CH2- . In the scheme above, reaction (1) represents water hydrolysis, reactions (2) and (3) are concerned with carbonic acid and bicarbonate formation, respectively. Reaction (4) represents the Zwitterion formation and reaction (5) is base catalysis. The two latter reactions are highly coupled as carbamate and protonated amines are tightly bonded. Therefore, reaction (4) and (5) can be shown abstractly as:

$$CO_2 + 2RNH_2 \leftrightharpoons [RNHCO_2^- + RNH_3^+] \quad (7)$$

Reaction (7) is a reversible acid-base neutralization reaction. In this reaction, absorption of CO_2 in alkanolamine solvent is exothermic; hence, it is possible to liberate CO_2 by heating the CO_2-rich solvent mixture and driving the reaction to left. Therefore, in theory, it is possible to regenerate the alkanolamine and recycle it for reuse in the absorber. In practice, a small amount solvent make-up is supplied to compensate the losses associated with the solvent escape and degradation reactions.

Various thermodynamic models were proposed by researchers in order to describe the thermophysical properties of the mixture of CO_2 absorbed into alkanolamines. These methods can be broadly categorized to non-rigorous and rigorous methods. In non-rigorous methods, equilibrium constants are considered for the aforementioned reactions and are reconciled against experimental data. The major drawback of non-rigorous methods is the lack of precision for closing energy balances and predicting speciation of components [17]. In addition, the rigorous methods can be classified to (1) activity-based models (derived from Gibbs free energy), and (2) equation of state models (derived from Helmholtz free energy). A frequently used activity-based model is Electrolyte Non-random two-liquid model (E-NRTL) in which the activity coefficient expressions of the original NRTL model are modified, and certain constraints regarding local like-ion repulsion and electroneutrality are imposed (Chen and Song, 2004). An alternative activity based model is the Extended UNIQUAC model where the original UNIQUAC model was modified to account for ionic interactions (Faramarzi et al., 2009). A limitation of the aforementioned activity-based models is that they only describe the liquid phase and a separate equation of state (e.g., Soave–Redlich–Kwong equation of state by Faramarzi et al., 2009) should be applied for modelling the vapour phase. Alternatively, researchers attempted to use

equations of states which can consider the presence of ionic components (Huttenhuis et al., 2008). More recently, application of equations of state which are able to accommodate chemical equilibria such as association between molecules, has been the focus of various research groups (Fürst and Renon, 1993; Button and Gubbins, 1999). Here, the treatment is based on statistical associating fluid theory (SAFT), in which the free Helmholtz energy is correlated to the intermolecular association between the molecule segments (Chapman et al., 1989; Mac Dowell et al., 2010):

$$\frac{A^{mix}}{NkT} = \frac{A^{IDEAL}}{NkT} + \frac{A^{MONO}}{NkT} + \frac{A^{CHAIN}}{NkT} + \frac{A^{ASSOC}}{NkT} \quad (8)$$

In above, N refers to the number of molecules, k is the Boltzmann constant and T is the mixture temperature. On the right-hand-side, the first term represents the ideal Helmholtz free energy and the three other terms refer to the residual contribution due to monomers interactions, formation of chains, and intermolecular interaction between associating sites. Then, given the Helmholtz free energy of the mixture, A^{mix}, it is possible to calculate other mixture properties (e.g., $\mu_i = (\delta A/\delta N_i)_{T,V,N_{i\neq j}}$). The association contribution is based on thermodynamic perturbation theory (TPT) (Wertheim, 1984), where by using intermolecular potential models (e.g., square well with variable range) and by adjusting their parameters (well depth and range), it is possible to fully characterize the strength of the associating sites.

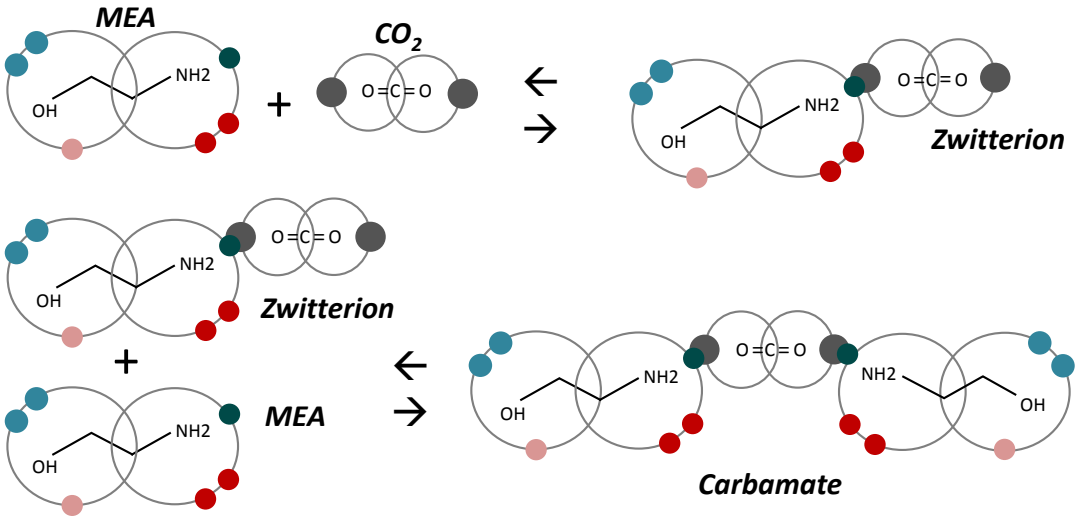


Fig. 2. Schematic representation of Carbamate formation

The idea is shown in Fig. 2 for the case of reaction (4) and (5), (Mac Dowell et al., 2010). In the new approach, the rate of reactions, the concentration of intermediate zwitterion, and its thermophysical properties are not formulated anymore. Instead, CO_2 and MEA are represented as associating molecule chains with two and six

associating sites, respectively. Then, the concentration of CO_2 in association with two MEA molecules represents the actual CO_2 loading of the solvent at different temperatures and pressures. The combination of rate-based modelling and representation of chemical reactions using statistical associating fluid theory (SAFT) provides a consistent modelling approach. The justification is that for solvents such as MEA and GCCmax, the rate of reaction is significantly faster than the heat and mass transfer phenomena. Therefore, the knowledge of the rate of reactions at the gas-liquid interface is unnecessary and the chemical equilibrium sufficiently describes the actual physical system behaviour. It is notable that in the case of solvents for which the reaction kinetics are not fast enough, this modelling approach may introduce approximations.

This modelling approach offers several advantages; firstly unlike activity-based models, the same equation of state is used to describe both liquid and vapour phases. Secondly, the chemical equilibria are treated at the same level as phase equilibria. Furthermore, this approach results in significant model reduction because the speciation of intermediate ions is not included in the mathematical formulation and the uncertainties associated with their thermophysical parameters are disentangled from problem formulation. Most of all, the aforementioned approach establishes a connection between the chemical and physical behaviour of the mixture and the molecular structure of the involved materials. This is of particular importance to new solvents as the required information can be acquired from the available data for the molecular segments of associating sites from literature experimental data.

In the present research, rate-based gas-liquid contactors were developed based on a combination of two-film theory and statistical associating fluid theory for potentials of variable range (SAFT-VR). The applied software tools were advanced modelling library gas-liquid contactors (AML-GLC) and gSAFT toolboxes developed by Process System Enterprise Ltd (PSE). The parametric values of thermodynamic models for the GCCmax solvent are obscured in order to respect the confidentiality agreements with Carbon Clean Solutions Limited (CCSL) and Process System Enterprise (PSE). The underlying mathematical modelling of the gas-liquid contactors were similar to (MacDowell et al., 2013). The SAFT thermodynamic model and its application for modelling CO_2 capture solvent are described by MacDowell et al., (2010).

3. Pilot plant operation and model validation

In order to ensure effective benchmarking and model validation, two sets of pilot plant runs were conducted using the monoethanolamine (MEA) and GCCmax solvents. MEA served as the baseline reference solvent. The

pilot plant studies were conducted in the US National Carbon Capture Center (NCCC) located in Alabama, USA. The capture process is shown in Fig. 3, which is based on a more detailed process flow diagram in (Gayheart et al., 2013). The column specifications for the capture process in the National Carbon Capture Center (NCCC) are reported in Table 1. The process description is as follows. Firstly, the pressure of the pre-scrubbed and cooled flue gas is increased via a blower and then is sent to the absorber column. In the absorber column, flue gas is brought in contact with the lean solvent, and the CO_2 is chemisorbed into the solvent. The absorption process is exothermic and the released heat increases the solvent temperature. The solvent enriched with the absorbed CO_2 is sent to the desorber column where the carbon dioxide is released through heating. Before, recycling the hot lean solvent to the absorber column for reuse, there is an opportunity for heat integration to the rich solvent. Additional cooling will be provided using cooling water. The solvent and water losses are compensated with adequate make-ups.

Table 1. Column Specifications (Gayheart et al., 2013).

Column	Packing	Height of each bed (m)	Diameter (m)	Number of beds
Absorber	Mellapakplus M252Y- Steel	6.1	0.66	3
Desorber	Mellapakplus M252Y- Steel	6.1	0.61	2

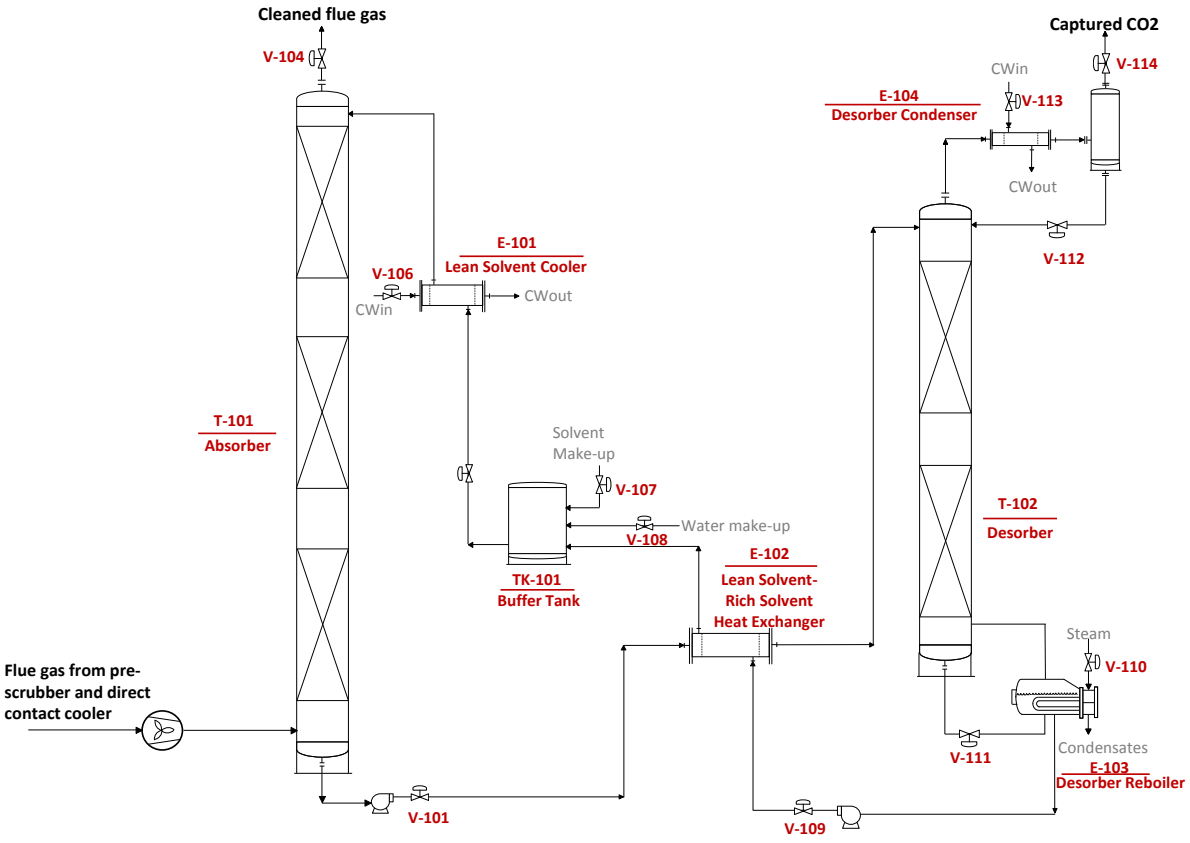


Fig. 3. A representative flow diagram of the US Natural Carbon Capture Center (NCCC) CO_2 capture pilot plant, Alabama, US (Gayheart et al., 2013).

271 Table 2 shows the results of model validation. Since the NCCC pilot plant was not previously operated under
272 natural gas exhaust conditions, the model validation was conducted based on historical data for a scenario of
273 coal-fired exhausts. The last column in Table 2 reports the prediction of the model, when the process is
274 operated under natural gas exhaust conditions. Table 2 shows a very good agreement between pilot plant data
275 and simulation results, in terms of captured CO_2, and the solvent composition. Minor discrepancies in the
276 consumed steam are deemed to be associated with heat losses and temperature indicator errors. Table 3
277 reports the results of the GCCmax solvent model validation under natural-gas-fired conditions. Two sets of
278 pilot plant data were used, which essentially are different with respect to the lean solvent temperature
279 entering the absorber top. The justification was due to the fact that in different parts of the world, cooling
280 water may be supplied at different temperatures. Again the model predictions are in very good agreement
281 with the pilot plant data with respect to the captured CO_2 and the solvent concentrations, giving confidence in
282 the model's predictive capabilities. Minor discrepancies in the required steam and temperatures were
283 attributed to lack of insulation or temperature measurement errors.
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286 **Table 2. Model validation for MEA baseline solvent.**

		Alabama-coal	Alabama-coal	Alabama NG
		Pilot Plant	Simulation	Simulation
Flue gas to the absorber				
Nitrogen + Oxygen	Mass Fraction	0.786	0.786	0.909
Carbon Dioxide	Mass Fraction	0.165	0.165	0.067
Water	Mass Fraction	0.049	0.049	0.024
Total flowrate	kg/s	0.628	0.628	0.628
Flue Gas Temperature - Absorber Inlet	K	316.56	316.56	316.56
Lean Solvent - Absorber Inlet				
Amine	Mass Fraction	0.297	0.298	0.296
CO_2	Mass Fraction	0.063	0.059	0.059
Water	Mass Fraction	0.640	0.643	0.645
Total	kg/s	2.52	2.51	1.3
Lean solvent temperature	K	316.15	316.15	316.15
Intercoolers outlet temperature	K	316.15	316.15	-
Reboiler Steam				
Steam pressure	bar	2.92	2.92	2.92
Steam temperature	K	405.6	405.6	405.6
Steam flowrate	kg/s	0.18	0.15	0.07
Lean-Rich Heat Exchanger				
Lean in	K	388.87	388.9	389
Lean out	K	331.4	338.9	330.8
Rich in	K	327.91	330.4	321.7
Reboiler temperature	K	385.6	388.0	389.0
Absorber bottom pressure	bar	1.1	1.17	1.16
Absorber top pressure	bar	1.04	1.04	1.04
Desorber bottom (reboiler) pressure	bar	1.71	1.71	1.16
Desorber top pressure	bar	1.69	1.70	1.70
General specifications				
CO_2 capture efficiency	%	91.84	91.85	90
Inter-stage Cooling		Yes	Yes	No

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288 **Table 3. Model validation for GCCmax solvent.**

		Data Set 1	Data Set 1	Data Set 2	Data Set 2
Absorber inlet gas stream		Pilot Plant	Simulation	Pilot Plant	Simulation
Nitrogen + Oxygen	Mass Fraction	0.895	0.895	0.896	0.896
Carbon dioxide	Mass Fraction	0.065	0.065	0.065	0.065
Water	Mass Fraction	0.040	0.040	0.039	0.039
Temperature	K	313.1	313.1	312.8	312.8
Total flowrate	kg/s	0.995	0.995	0.9951	0.9951
Absorber					
Absorber top pressure	bara	1.160	1.160	1.160	1.160
Absorber bottom pressure	bara	unavailable	1.224	unavailable	1.221
Absorber outlet CO_2 concentration	Mass Fraction	0.0053	0.0056	0.004	0.005
Lean solvent - absorber inlet temperature	K	304.1	304.1	325.4	325.4
Rich solvent - absorber outlet temperature	K	318.1	316.5	318.7	316.1
Lean solvent flowrate	kg/s	0.857	0.857	0.756	0.756
Desorber (regenerator)					
Desorber Bottom Temperature	K	388.6	388.6	395.4	395
Desorber Top Pressure	bara	1.701	1.708	2.031	2.03
CO_2 stream	kg/s	0.0578	0.0611	0.060	0.0605
Reboiler Steam					
Steam pressure	bar	3.606	3.605	4.075	4.075
Steam temperature	K	402.8	402.8	408.5	408.5
Steam condensate Temperature	K	401.9	401.9	407.8	407.5
Steam flowrate	kg/s	0.091	0.078	0.086	0.0823
Lean-Rich Heat Exchanger Temperatures					
Lean solvent in	K	387.4	388.6	394.2	395.0
Lean solvent out	K	325.0	322.6	324.7	327.4
Rich solvent in	K	318.9	316.5	319.9	316.1
Rich solvent out	K	380.4	379.9	384.0	379.9
Lean solvent concentration					
GCCmax Solvent	Mass Fraction	0.410	0.410	0.439	0.439
Water	Mass Fraction	0.536	0.541	0.504	0.515
CO_2	Mass Fraction	0.054	0.049	0.057	0.046
General specifications					
CO_2 Capture Efficiency	%	89.1	91.7	92.50	92.13
Inter-stage Cooling		No	No	No	No

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The validated pilot plant model was used to extract several technical key process indicators (KPIs) which are important measures that quantify the difficulties associated with CO_2 separation from the flue gas in terms of the required heating and cooling duties, required packing, and solvent circulation. These measures are scaled with respect to the amount of pure CO_2 captured, to become independent of the pilot plant throughput and enable comparisons. Table 4 provides the comparisons between the solvents. This table reveals that compared to the MEA reference solvent, the GCCmax solvent requires 25.4-29.4% less steam for solvent regeneration in the reboiler, per ton of CO_2. In addition, compared to the MEA reference solvent, the GCCmax solvent requires 73-84.4% less cooling water in the condenser and intercooler. The volume of packing in the absorber and desorber columns also shows improvements in the case of the GCCmax solvent. Finally, the GCCmax solvent circulation is 58.8-64.7% less than MEA solvent circulation which implies significant reductions in the electricity power needed for solvent pumping.

Table 4. Key process indicators (KPIs) for the GCCmax solvent and baseline MEA solvent

Key Process Indicators (KPIs)	Unit	**MEA**	**GCCmax (Data1)**	**GCCmax (Data2)**
Heating duty	(MJ/ton CO_2)	3986	2813	2975
Cooling duty	(MJ/ton CO_2)	5644	1524	884
Volume of packing	(m3/ton CO_2 hr-1)	46.619	45.64	45.91
Solvent circulation flow rate	(ton solvent/ton CO_2)	34	14	12

4. Solvent performance optimization

The last part of the present research was concerned with model-based optimization of the carbon capture process. Having validated the process model using pilot plant data, we wished to explore the improvement opportunities and the significance of various investment and operational decisions. Three scenarios were studied:

In Scenario (1), the dimensions of process equipment and operating conditions were optimized simultaneously. This scenario represents the case where the plant is built for the first time.

In Scenario (2), the dimensions of process equipment are fixed and only the operating conditions are optimized. This study is concerned with the scenario where an existing process is adapted to a new solvent.

In Scenario (3), similar to the second scenario, the dimensions of process equipment are fixed. However, operating conditions and the GCCmax solvent blend composition are optimized simultaneously. This scenario highlights the implication of the solvent optimization for energy saving.

In the first scenario, the objective function was the Total Annualized Costs because:

$$Total\ Annualized\ Costs = \frac{Fixed\ Capital\ investment}{Plant\ effective\ Life} + Total\ Annual\ Energy\ costs \qquad (9)$$

However, since in the second and third scenarios the equipment dimensions are fixed, the first right-hand-side term of the above equation is constant and only Total Annual Energy Costs are optimized. In equation (9), the value of 5 years were considered for the plant life cycle, in order to incorporate interest rate and the time value of money. The costs of process equipment were calculated according to the costing correlations provided in (Couper et al., 2012). Lang factor of 6 was considered for estimating the total capital investment (Peters et al., 2004). The considered utility costs were 37.02 $/MWh for electricity (Electricity Wholesale Market 2015), 0.048 $/tonne for cooling water (Ulrich and Vasudevan, 2006), and 14.5 $/tonne for steam. Two additional constraints were considered:

$$Carbon\ capture\ = 90\% \qquad (10)$$

$$Reboiler\ temperature < 120\ ^{o}C \qquad (11)$$

The first constraint ensures that 90% CO_2 is captured from the flue gas. The second constraint limits the maximum reboiler temperature in order to avoid solvent degradation. Table 5 presents the results of optimization. A comparison between Scenario (1) in which process equipment was being optimized and the other two scenarios, suggests that the size of the pilot-plant absorber and desorber columns was larger than the required values. This is an intuitive observation, because pilot plants are often to an extent overdesigned in order to allow a variety of solvent testing. In the first scenario, the heating and cooling duties are slightly higher than the other two scenarios, as they were optimized in conjunction with capital investment. In the other two scenarios, the process equipment items were fixed and the optimizer took the opportunity to exploit process equipment for energy saving. It is notable that there is a significant energy saving when the solvent composition and operating conditions were optimized simultaneously, which illustrates the importance of solvent control and optimization during process operation.

339 **Table 5. Optimization results**

		Scenario (1)	Scenario (2)	Scenario (3)
Optimization objective function		Total annualized costs	Annualized energy costs	Annualized energy costs
Optimization variables		*Equipment size and operating conditions*	*Operating conditions only*	*Operating conditions and solvent composition*
Flue gas to absorber				
H2O	mass fraction	0.0388	0.0388	0.0388
CO_2	mass fraction	0.0651	0.0651	0.0651
N2	mass fraction	0.7320	0.7320	0.7320
O2	mass fraction	0.1640	0.1640	0.1640
Pressure	Pa	1.22E+05	1.22E+05	1.22E+05
Temperature	K	312.8	312.8	312.8
Flowrate	kg/s	0.995	0.995	0.995
Absorber diameter	m	0.5	0.66	0.66
Absorber height	m	9	18.3	18.3
Lean Solvent to absorber				
Flowrate	kg/s	0.787	0.874	0.739
Temperature	K	324.2	319.9	320.2
Composition				
H2O	mass fraction	0.5390	0.5390	0.5470
CO_2	mass fraction	0.0517	0.0517	0.0444
GCCmax	mass fraction	0.4093	0.4093	0.4086*
Reboiler temperature	K	398	398	398
Reboiler steam pressure	Pa	4.07E+05	4.07E+05	4.07E+05
Reboiler steam temperature	K	408.5	408.5	408.5
Reboiler Steam flowrate	kg/s	8.325E-2	7.22E-02	6.282E-2
Lean-Rich heat exchanger				
Lean in	K	398	398.0	398.0
Lean out	K	325.3	321.0	321.2
Rich in	K	317.6	316.3	317.2
Rich out	K	386.7	390.0	390.0
Condenser temperature	K	301.3	301.3	301.5
Desorber condenser duty	W	58909.5	49195.7	43096.1
Lean solvent cooler duty	W	2152.89	2374.1	1936.87
The total cooling duty	W	**61062.39**	**51569.8**	**45032.97**
The heating (Reboiler) duty	W	**176845**	**152554**	**132781**
CO_2 Capture		90%	90%	90%

340 * The mass fractions of the ingredients of the GCCmax solvent were optimized, with a variation of over 50% in
341 some mass fractions.

5. Conclusions

This paper presented integrated modelling and pilot plant studies in order to benchmark alternative carbon capture solvents, along with key performance indicators (KPIs) to support comparison. The proposed methodology was used to study the technical and energetic performances of GCCmax, a new amine-promoted buffer salt (APBS) solvent, developed by Carbon Clean Solutions Limited (CCSL). In order to obtain meaningful results, a high fidelity model was developed based on rate-based modelling of absorption and desorption columns, in addition to modelling thermodynamic and reaction phenomena based on statistical associating fluid theory (SAFT). The developed model was validated using pilot plant data, with very good agreements between predicted and reconciled data. Detailed comparisons were made based on several key process indicators which quantify the difficulties associated with CO_2 capture and include: the required heating duty, cooling duties, volume of column packing and the solvent circulation rate. The comparisons between key process indicators (KPIs) established the superior performance of the new GCCmax solvent in comparison with the MEA baseline solvent. The last part of this paper explored the opportunities for further improvement of the solvent performance via optimization. The studied scenarios were comprehensive and included (1) designing a new process, (2) retrofitting an existing process using a new solvent and (3) optimizing the solvent composition and the operating conditions of an existing process. While the presented methods are applied for the new GCCmax solvent and the MEA reference solvent, the research methodology is general in nature and can provide an effective standard for solvent comparisons.

The present research illustrated the application modelling and pilot plant studies for optimization of the solvent performance. In the future studies, we will apply the developed model for scale up and power plant integration based on the methodology of integrated process design and control (Sharifzadeh 2013a) using inversely controlled process models (Sharifzadeh 2013b; Sharifzadeh and Thornhill 2012, 2013).

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