Comparisons of Amine Solvents for Post-combustion CO_2 Capture: A Multi-objective Analysis Approach

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Abstract

Amine solvents are of great interest for post-combustion CO_2 capture applications. Although the development of new solvents is predominantly conducted at the laboratory scale, the ability to assess the performance of newly developed solvents at the process scale is crucial to identifying the best solvents for CO_2 capture. In this work we present a methodology to evaluate and objectively compare the process performance of different solvents. We use Aspen Plus, with the electrolyte-NRTL thermodynamic model for the solvent CO_2 interactions, coupled with a multi-objective genetic algorithm optimization to determine the best process design and operating conditions for each solvent. This ensures that the processes utilized for the comparison are those which are best suited for the specific solvent. We evaluate and compare the process performance of monoethanolamine (MEA), diethanolamine (DEA), and 2-amino-2-methyl-1-propanol (AMP) in a 90% CO_2 capture process from a 550 MW coal fired power plant. From our analysis the best process specifications are amine specific and with those specific, optimized specifications DEA has the potential to be a better performing solvent than MEA, with a lower energy penalty and lower capital cost investment.

Keywords: Carbon capture, Amine solvent comparisons, multi-objective optimization, Aspen Modeling

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1. Introduction

Aqueous absorption/stripping using amine solvents is regarded as one of the most promising first generation CO_2 capture technologies for large point sources, such as coal fired power plants. This process stands out over other CO_2 capture technologies due to a depth of process knowledge from decades of use in the natural gas and food processing industries and the versatility of implementation of the process as a retrofit to an existing plant or integrated within the design of a new plant (Rochelle, 2009). However, the high economic penalty associated with the process is one of the leading inhibitors to wide-spread commercialization. Ciferno et al. (2010) estimated that the current commercial process, using monoethanolamine (MEA), could lead to up to a 30% reduction in the overall efficiency of the power plant and a corresponding 80% increase to the cost of electricity.

Up to 70% of the parasitic energy demand of CO_2 capture using MEA is due to the thermal energy required for amine regeneration, with the next major contributor being the energy required for CO_2 compression (Herzog et al., 2009). As described by Oexmann and Kather (2010), the thermal energy requirement for amine regeneration is fixed by three heating demands, the heat required to break the amine-CO_2 bond, latent heating of the solvent, and the required amount of stripping steam, all of which depend on the amine-CO_2 interaction energy. This relationship has motivated research focused on developing new amines solvents that have a lower energy penalty for CO_2 capture through the combined impacts on those three heating loads.

Experimental (Puxty et al., 2009; Sartori and Savage, 1983; Singh et al., 2007, 2009; Yoon and Lee, 2003; Chowdhury et al., 2013) and molecular modeling (da Silva and Svendsen, 2007; Lee and Kitchin, 2012; Mindrup and Schneider, 2010) work show a relationship exists between amine molecular structure and the energy and kinetics of the amine-CO_2 reaction. At the experimental and modeling level, parameters such as the amine-CO_2 reaction energy, reaction rates, and the equilibrium CO_2:amine ratio for a solvent can be determined. However, given the complexity of the relationship between reaction energy and process energy demands, as described by Oexmann and Kather (2010), the parameters that can be measured experimentally do not translate simply into energy demands at the process level. Although experimental and molecular modeling work have shown that altering amine molecular structure can modify amine-CO_2 interactions, the question still remains of how these modifications impact energy demands at the process level, which is integral to identifying better CO_2 capture solvents.

Aspen Plus process models have been widely used as tools to study the CO_2 capture process and quantify process energy demands, with a majority of the existing work using MEA as the capture solvent. Early works used these models to determine energy and mass balances around each process unit for a fixed process with a specific focus on determining the overall energy demands (Alie, 2004; Freguia, 2002; Freguia and Rochelle, 2003). More recently, Aspen Plus models have been used to understand the relationship between operating conditions of the CO_2 capture process and energy demands, specifically the stripper reboiler heat duty. Parametric studies show that both equipment and process operating conditions, such as the CO_2 loading and temperature of the amine solvent entering the absorber, the absorber temperature, and stripper pressure, have a large impact on the stripper reboiler heat duty (Abu-Zahra et al., 2007; Oyenekan and Rochelle, 2007; Alie et al., 2005; Salkuyeh and Mofarahi, 2012). These studies illustrate the large multi-dimensional design space of a CO_2 capture process and highlight the necessity of determining the best conditions that minimize the energy demands, instead of arbitrarily setting them, when judging the performance of a process using a specific solvent.

Few studies have performed analysis of the CO_2 capture process using other amine solvents in addition to MEA (Chang and Shih, 2005; Dave et al., 2009; Oyenekan and Rochelle, 2006; Nuchitprasittichai and Cremaschi, 2011; Chakma et al., 1995). However, many of the approaches used in those works limit the ability to fairly compare the energy demands of the different solvents and understand the impact of changes in amine-CO_2 reaction energy on the process. Chakma et al. (1995) presented a parametric study examining the impact of design variables as well as the choice of solvent selection on the cost of CO_2 capture, in \$CAD/ton CO_2 captured. They performed the cost comparison for six different amine solvents considering the market price of each solvent, which unfairly biases solvents that currently have a large market demand. Additionally, it is unclear if any process optimization was performed for each solvent, or if a fixed process was used. Chang and Shih

(2005) modeled three design schemes for the CO_2 capture process using two different amines, MEA and a mixed diglycolamine/methyldiethanolamine (DGA/MDEA). Their analysis focused on identifying the major design variables for each amine, but they only performed a design optimization for the MEA. Similarly Dave et al. (2009) presented a comparison of the thermal energy requirements of amine regeneration of a fixed CO_2 capture process using MEA, DGA (diglycolamine), and AMP (2-amino-2-methyl-1-propanol). The process operating conditions used for all the amines were those optimized for 30 wt.% MEA. Utilizing a fixed design and operating conditions of a process to compare the performance of different amines, obscures their true performance differences due to changes in amine-CO_2 chemistry and the results likely do not present the amine in the best light. Numerous process models of the MEA system have shown the significant effect of different operating conditions on the energy demands of the process. Additionally, each amine has a different chemistry with CO_2, which would likely lead to different optimal process operating conditions. Thus, it important to model the CO_2 capture process using conditions best suited for the capture solvent.

Nuchitprasittichai and Cremaschi (2011) present a simulation-optimization approach using response surface optimization methods to analyze the impact of different amine solvents, solvent concentration, absorber and stripper column heights, and operating conditions on the \$/ton of CO_2 captured of a post-combustion capture process. The optimization approach allowed the evaluation of the cost of CO_2 capture with each amine using the conditions best suited for that amine. However, their analysis only focused on the cost of CO_2 capture in the optimization, and did not consider the impact of the capture process on the overall plant net power output, which is the performance measure that is most affected by amine-CO_2 chemistry of different solvents. Additionally, performance criteria on the capture process, i.e. 90% CO_2 capture (the target set by the DOE), was not imposed on their model. A sensitivity analysis of CO_2 flue gas concentration and utility costs on the cost of CO_2 capture using similar methods in Nuchitprasittichai and Cremaschi (2013).

This work addresses an existing gap in understanding of the impact of solvent selection on the post-combustion CO_2 capture process by presenting a framework to analyze and compare the energy penalty and capital cost demands of a CO_2 capture process using different amine solvents. The CO_2 capture process is modeled in Aspen Plus using a fixed process flowsheet. The process models are coupled with a multi-objective genetic algorithm that sampled a defined design space of process and operating conditions to determine sets of conditions that were best suited for each solvent to meet design objectives that maximize net power output of the overall power plant and minimize the capital cost investment of the CO_2 capture process. A traditional optimization approach could be used to determine the optimum point within the design space with respect to the design objectives. However, as highlighted in the work of Eslick and Miller (2011), the multi-objective genetic algorithm approach results in a set of near optimal Pareto solutions.

This solution set provides information about the behavior of the system near optimal conditions and about the associated trade-offs between design objectives. We present the multi-objective analysis for three amine solvents: MEA, DEA, and AMP. Comparisons of the Pareto front for each amine shows the impact of solvent selection on the process and can be utilized to identify better performing amines.

2. Materials and Methods

2.1. Process Description

In a post-combustion CO_2 capture process, the flue gas from the power plant is pre-cooled in a contact condenser and compressed slightly before entering the CO_2 absorber. In the absorber, CO_2 reacts with the amine solvent (Lean Amine), leaving a CO_2 lean overhead flue gas stream that can be emitted to the atmosphere. The amine rich in CO_2 (Rich Amine) is pre-heated in a crossflow heat exchanger, with the stripper bottoms as the heating stream. The pre-heated Rich Amine stream is passed to the stripper. There, CO_2 is thermally driven out of the solvent stream, regenerating the amine and producing a moisture rich CO_2 overhead stream. The CO_2 is dried and compressed to pipeline conditions in the compression unit. Schematics of the CO_2 capture and compression process considered in this work are shown in Figure 1 and Figure 2 respectively. The direct contact condenser is shown as part of the CO_2 capture process, but is not included in the analysis in this work because it is a flue-gas pretreatment unit. The heat capacity of the flue gas is much lower than that of the solvents, and we assume that small variations in the flue gas inlet temperature do not significantly affect the absorber performance or size. One could consider the tradeoff in capital cost of a larger direct contact condenser to achieve a lower flue gas inlet temperature, but that was not considered in this work. The CO_2 compression unit is included because the energy of compression accounts for a substantial portion of the power plant energy penalty due to CO_2 capture and the compression energy also depends on the outlet conditions of the stripper, which is impacted by the amine-CO_2 chemistry (Oexmann and Kather, 2010).

2.2. Aspen Plus Process Models

Process models were developed using Aspen Plus v7.2 (2010) and the electrolyte-NRTL thermodynamic model with the electrolyte property inserts for each amine. The flue gas flow rate and composition entering the absorber were taken from the NETL (2010) bituminous baseline report for a 550 MW supercritical pulverized coal power plant. For each amine, the amine solvent composition was fixed at 11 mol% amine basis, which is equivalent to 30 wt% MEA. Although corrosivity and viscosity of the amine will factor into the molar concentration of amine in actual applications, since the purpose of this study was to assess the impact of changes to the amine-CO_2 chemistry on process performance, a fixed amine mol% basis was used for all amines in these models. This was fixed to keep the number of available reacting molecules constant and ensure that any differences in process performance were only an effect of different chemistries.

The absorber was modeled using the rate-based RadFrac tower model, with a 1.524 m (5 ft) water wash section and an absorbing section, using Sulzer MellapackPlus 252Y packing and 30 discretization sections. An intercooler was included in the lower section of the absorber, drawing off hot liquid from a section and returning cooled liquid to the section below. The absorber was designed to remove 90% of the CO_2 in the flue gas stream and sized for 80% flooding. The stripper was also modeled using a rate-based RadFrac tower model, using Sulzer MellapackPlus 252Y structured packing, 22 discretization sections, a kettle reboiler, and a partial vapor condenser. The stripper was designed to regenerate the amine to the lean amine CO_2 loading specifications and sized for 80% flooding. The height height of the absorber and stripper were manipulated variables set by the multi-objective optimization discussed Section 2.4.

The heat exchangers in the CO_2 capture process were designed as shell and tube heat exchangers. The lean-rich heat exchanger was designed with a 13.9 °C (25 °F) temperature approach between the rich amine stream from the absorber and the lean amine stream from the stripper. The amine trim cooler was designed to cool the lean amine stream back to absorber inlet conditions.

The CO_2 compression unit was modeled using 10 compression stages with two intercoolers. The process was designed to compress and dry the CO_2 gas stream from the stripper overhead to pipeline transport conditions: 15.27

MPa (2215 psi) and 310 K (100 °F) (NETL, 2010).

2.3. Process Performance Parameters

Net power output and capital cost were used in this work as performance metrics for the CO_2 capture process. Net power output was used as the energy metric instead of thermal energy demand in the stripper reboiler because it is a more complete measure of impact on power plant product and includes the pumping and compression costs (Oyenekan and Rochelle, 2007). Net power output for the coal power plant with CO_2 capture was calculated as the gross power output from a 550 MW power plant with reduced low pressure steam feed, determined from a surrogate model as described in Eslick and Miller (2011), less the energy demands from CO_2 compression and amine circulation. The model is detailed in the supporting information. The reduced steam feed was determined by calculating the necessary low pressure saturated steam draw at 274.5 kPa to meet the thermal energy demand in the stripper reboiler.

The equipment size and capital cost were determined using Aspen Plus model results and sizing and costing functions from Seider et al. (2008). The capital cost was calculated as the free on board (F.O.B) cost using the Lang method, with a CE factor of 550 as described in Seider et al. (2008). Solvent costs were not included in the capital cost.

2.4. Multi-objective Analysis

As previously discussed, when modeling and comparing performance of a CO_2 capture process using different amine solvents, it is important to model each amine using a set of operating conditions that are best suited for that amine. In this work we selected net power output and capital cost as the optimization variables, and we note that different objectives (e.g. minimization of water usage) may lead to different operating conditions that optimize those objectives. The multi-objective analysis approach used a NSGA-II genetic algorithm to probe the design and operating space with the objective of optimizing the performance parameters. The optimization was implemented in modeFRONTIER v4.4.2 (2012), an optimization and data analysis software package. The Aspen Plus process models were interfaced with modeFrontier through Excel, using the Sinter simulation interface (Eslick and Miller, 2011; Carbon Capture Simulation Initiative, 2012)

The genetic algorithm sought to minimize the capital cost and maximize the net power output of the CO_2 capture process for each amine. Both design and process operating conditions were considered as design variables. The design space for the genetic algorithm is listed in Table 1. The algorithm was seeded with 25 cases determined using a Latin hyper cube distribution across the design space as the initial generation. The genetic algorithm was carried out for 150 generations on a 2.93GHz Core 2 Duo PC and took about a week to finish for each solvent.

3. Results and Discussion

3.1. Analysis of the MEA Process

We first discuss the results from the genetic algorithm analysis of the CO_2 capture process using 11 mol% MEA as the capture solvent. The 150 generations of the genetic algorithm yielded about 3000 converged and feasible Aspen Plus solutions for the CO_2 capture and compression process, each with different design and operating conditions and corresponding capital cost and power output. The cases that did not yield solutions either failed to converge or led to infeasible results with the reboiler temperature being greater than the available low pressure steam temperature (403.65 K, 279.8 kPa). Although thermal amine degradation is known to occur in the stripper (Davis and Rochelle, 2009), the reboiler temperature was not constrained to minimize this. Amine degradation would impact operational costs of the process, but it is outside the scope of this work.

Figure 3 shows the results of the converged cases (a few irrelevant cases are outside the boundaries of the figure) leading to higher power output and lower capital cost. Raw data for all cases can be found in the supporting information. The Pareto front (filled circles) shows the relationship and trade-offs between the two design objectives. There is a minimum capital cost to capturing 90% CO_2 from a 550 MW flue gas stream and a maximum possible net power output given the MEA-CO_2 chemistry and defined process. The Pareto front shows that increasing the plant efficiency comes with increased capital cost, due to larger equipment. However, there becomes a point such that only marginal gains in plant efficiency are seen with additional capital investment. This analysis provides a better understanding of the limitations of the CO_2 capture process and can be utilized in decision making during project design.

Table 2 shows two cases that optimized each design variable independently, i.e., maximizing power output, and minimizing capital cost. Case 1 shows that the highest power output is achieved with moderate lean amine CO_2 loading and high stripper condenser pressure. The moderate lean loading is consistent with other parametric studies of lean amine loading on energy demands of CO_2 capture (Abu-Zahra et al., 2007; Oyenekan and Rochelle, 2006). Additionally, the high stripper operating pressure is consistent with process heuristics (Brennecke and Gurkan, 2010; Oyenekan and Rochelle, 2007).

3.2. The Effect of Solvent Selection

To emphasize the importance of selecting process operating conditions that are specific to each amine, we performed a single case model evaluation using the operating conditions that led to the highest power output from the MEA analysis (Case 1), substituting MEA with AMP and DEA. The results, presented in Table 3, show that both AMP and DEA have a larger negative impact on the power output, though the capital cost for the process is lower in each case. This analysis could lead to the conclusion that MEA is the superior CO_2 capture solvent (in terms of power output), though AMP is superior in terms of capital cost. However, this is misleading because no consideration has been made to account for the effects of amine-CO_2 chemistry on the design and operating conditions.

Using the genetic algorithm optimization, the design space is sampled to identify the best conditions for each amine. In the analysis with DEA and AMP, Pareto fronts were identified for both solvents (Figure 4). The relationship between capital cost and net power output using DEA and AMP as the capture solvent is similar to MEA, i.e., there are trade-offs between the two design objectives. Additionally, combinations of design and operating parameters can be identified for both solvents that enable the DEA and AMP systems to capture 90% CO_2 from a 550 MW power plant with a higher net power output and lower capital cost investments compared to MEA.

The gain in power output and reduction in capital cost seen with the CO_2 capture process using DEA and AMP is predominantly due to a lower stripper reboiler heat duty. With a lower heat duty, less steam is required to regenerate the amine, leading to an increase in steam available for power generation (Figure 5). Additionally, the lower steam flow rate reduces the size of the kettle reboiler, which dominates the cost of the stripper process (Figure 6). These results show that minimizing the reboiler heat duty is a good design objective for minimizing energy demands and capital cost of the CO_2 capture and compression process.

The reboiler heat duty is a measure of the energy required in the stripper to perform the separation work necessary to regenerate the rich amine back to the lean amine CO_2 loading. The degree of separation is the working capacity of the amine ($\Delta\alpha$)(Equation 1). The relationship between the working capacity of the solvent and the reboiler heat duty is shown in Figure 7-A.

$$\begin{gathered}\Delta\alpha = \alpha_{rich\,amine} - \alpha_{lean\,amine} \\ \alpha_i = \frac{n_{CO_2,i}}{n_{amine,i}}\end{gathered} \tag{1}$$

As discussed previously, the reboiler heat duty accounts for the energy to break the amine CO_2 bonds, as well as the stripping steam and latent heating requirements. Equation 2 shows this as the sum of two enthalpies, an enthalpy of reaction and a process enthalpy. Assuming the latent heating requirement is nominal due to heat recovery in the cross heat exchanger, the process enthalpy demands are dominated by the vaporization of water to generate stripping steam.

$$\Delta H_{Reboiler} = \Delta H_{rxn} + \Delta H_{Process} \tag{2}$$

Using the experimentally measured reaction enthalpies reported in Chowdhury et al. (2011), the process enthalpy demands for each solution can be determined (Figure 7-B). These results along with what is known experimentally about these amines (Figure 8) provide insight to tuning amines in order to minimize the reboiler heat duty.

Amines are known to interact with CO_2 along two pathways, through the formation of a bicarbonate species utilizing a 1:1 amine to CO_2 ratio, and a carbamate pathway with a 2:1 amine to CO_2 ratio. The carbamate pathway has a higher reaction enthalpy than the bicarbonate pathway, and therefore is more energetically favorable. Unhindered primary and secondary amines, like MEA and DEA, interact with CO_2 along both the carbamate and bicarbonate pathway. Tertiary and hindered amines, like AMP, only interact with CO_2 along the bicarbonate pathway.

The results of this study show that the working capacity of DEA is higher than that of MEA at the optimal process conditions and the higher working capacity leads to a lower reboiler heat duty. Since the number of available reacting molecules is constant for all amines in this study, a higher working capacity could indicate that the carbamate pathway in DEA is less stable compared to MEA, thus favoring the 1:1 bicarbonate pathway. This conclusion is consistent with the heat of reaction presented in Figure 8 and stability studies performed by Sartori and Savage (1983) showing that carbamates are six times less stable in DEA than MEA. Thus, tuning the molecular structure of unhindered amines to destabilize carbamate formation could lead to a lower reboiler heat duty and a more optimal CO_2 capture process.

The AMP results suggest that hindered and tertiary amines fall along a different working capacity/reaction enthalpy relationship. Figure 8 shows that the reaction enthalpy and kinetics of AMP are close to that of DEA. However, the working capacity of the Pareto front solutions are closer to that of MEA. The single pathway interaction must limit the working capacity of AMP. Although the working capacity of AMP is limited, Figure 7-B suggests that AMP requires less stripping steam to regenerate the solvent and the reboiler heat duty is lower. Therefore, if a tertiary or hindered amine could be designed to have a high working capacity like DEA, it may result in a lower reboiler heat duty because of a lower stripping steam demand.

4. Conclusion

In this work we presented a methodology to evaluate and compare the performance of different amines as CO_2 capture solvents for a 550 MW power plant using net power output and capital cost of the CO_2 capture process as performance metrics. Using Aspen Plus to model the process and the NSGA-II genetic algorithm to identify a Pareto front of the the best design and operating conditions for each process that minimized capital cost and maximized power output, we observed a large set of possible solutions. The Pareto front for each amine illustrates the trade-offs between the two conflicting objectives. Additionally, comparing the Pareto fronts of each amine, we see that DEA has the potential to be the best solvent compared with MEA and AMP, for CO_2 capture.

The process analysis approach that we describe captures the effects of different amine chemistries on the CO_2 capture process. This approach and subsequent results can be utilized to focus the direction of solvent design by enabling the evaluation and comparison of contextually relevant performance metrics, instead of relying on only values measured at the laboratory level. However, the quantitative results from this work are highly dependent on the robustness of the thermodynamic models for the amine-CO_2 systems available in Aspen. Therefore, as the development of new solvents progresses, it will become increasingly important for research to include refining thermodynamic models for the solvents.

DISCLAIMER

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Figure 1: Simplified process flow digram of amine based post-combustion CO_2 capture process.

Figure 2: Simplified process flow diagram of CO_2 compression process.

Figure 3: Solutions from genetic algorithm analysis for a post-combustion CO_2 capture process using MEA solvent. Pareto front solutions denoted as filled circles.

Figure 4: Solutions from genetic algorithm analysis for the post-combustion CO_2 capture process using MEA, AMP, and DEA solvents. Pareto front solutions for each amine are denoted with filled symbols.

Figure 5: Reboiler heat duty [MW] versus net power output [MW] for Pareto front solutions from MEA, DEA, and AMP analysis.

Figure 6: Capital cost breakdown of Pareto front solutions for absorber, stripper, and CO_2 compression units for the MEA (a) and DEA (b) CO_2 capture process.

Figure 7: (A) Relationship between amine working capacity and total reboiler heat duty for Pareto front solutions of MEA, DEA, and AMP analysis. (B) Relationship between amine working capacity and process enthalpy component of reboiler heat duty (Equation 2 for Pareto front solution of MEA, DEA, and AMP analysis.

Figure 8: Experimentally measured heats of reaction and reaction rates for amine solvents. Adapted from Chowdhury et al. (2011).

Variable [units]	**Bounds**
Absorber	
Lean amine temp. [K]	[316.5, 333.15]
Lean amine loading [mol CO_2/mol amine]	[0.05, 0.35]
Absorber packing height [m]	[4.6, 13.7]
Intercooler draw stage	[23, 32]
Intercooler ΔT [°C]	[0, -10]
Stripper	
Regenerator packing height [m]	[3, 12.2]
Condenser pressure [kPa]	[137.9, 275.8]
Condenser temp. [K]	[316.5, 333.15]
CO_2 Compression	
Cooler 1 outlet temp. [K]	[311, 322]
Cooler 2 outlet temp. [K]	[311, 322]

Table 1: Equipment and process operating optimization variables.

Results	**Case 1**	**Case 2**
Power output [MW]	394.2	363.5
Capital cost [$M]	517.3	244.1
Reboiler temperature[K]	400	384
Working capacity ($\Delta\alpha$)	0.315	0.222
Model Inputs		
Lean amine temp. [K]	332.5	332.4
Lean amine CO_2 Loading [n_{CO2}/n_{amine}]	0.188	0.258
Absorber height [m]	13.56	4.69
Intercooler draw stage	31	24
Intercooler T [°C]	-9.89	-9.89
Regenerator height [m]	12.1	3.17
Condenser pressure [kPa]	222.01	138.58
Condenser temp. [K]	316.6	316.5
Cooler 1 outlet temp.[K]	312.9	311.2
Cooler 2 outlet temp. [K]	311.15	311.03

Table 2: Best solutions meeting individual design objectives using MEA in the post-combustion CO_2 capture process. Case 1: Maximum power output, Case 2: Minimum capital cost.

	MEA	**DEA**	**AMP**
Power Output [MW]	394	373	364
Capital Cost [$M]	517	362	353

Table 3: Single Aspen Plus process model evaluations of MEA, DEA, and AMP post-combustion CO_2 capture process using equipment and process design specification of Case 1.