

# **An Evaluation of General “Rules of Thumb” in Amine Sweetening Unit Design and Operation**

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## **ABSTRACT**

Many “rules of thumb” are widely used in the design and operation of amine sweetening units. These rules have been developed over the years and most engineers accept them even though many have little familiarity with how important they may or may not be. Few ask why we have these rules, how absolute they are, and whether the rules have any flexibility. In this paper, several of these rules are described and evaluated for their usefulness and necessity using parametric studies with a steady-state process simulator. The rules evaluated include the 5 C temperature approach in the absorber, the 0.12 kg/L specification for reboiler steam, the 99C lean/rich exchanger outlet temperature, and the regenerator pressure/reboiler temperature guideline. Although these four rules of thumb are excellent starting points, none of them represent optimum conditions for all cases and, depending on the situation, violating these rules could offer considerable advantages to process efficiency. Every situation is different and requires a thorough investigation as to whether changes to these set points are beneficial and whether these benefits offset any additional risks.

## **Introduction**

Amine sweetening units have been used in gas processing for nearly 80 years to remove H<sub>2</sub>S and CO<sub>2</sub> from sour gas streams.[1] Development first began with TEA and later moved to more advantageous amines such as MEA and DEA. During the last 20 years MDEA has become a more popular solvent, especially when used for selective removal of H<sub>2</sub>S over CO<sub>2</sub>. Specialty blends of MDEA with the addition of various additives to enhance performance have also become commonplace in industry.

Over the years of development various guidelines, rules of thumb, and design practices have evolved. Many designers take these rules for what they are, seldom stopping to ask how applicable they are to today's designs. Some guidelines have been in place longer than some solvents, such as MDEA, have been in general service. With the considerable differences between past and present solvent performance the question must be raised by the designer whether these guidelines are appropriate.

While there is a plethora of design rules, a few specific ones come to mind and should be reviewed. The need to have a 5C (10F) temperature approach between the gas and solvent feeds, for example, has existed for a number of years. Likewise the 0.12 kg/l (1 lb/gal) steam ratio rule, the 99C (210F) lean/rich exchanger outlet temperature guideline (on the rich side), and the required reboiler pressure/temperature have all been used for years, regardless of the amine type or the situation.

If there is one rule of thumb that is always true in gas processing, it is that every situation is different. In this study the above listed guidelines are investigated for their efficacy and usefulness. While deviating from well established operating points poses some risk, a thorough analysis can provide the designer or unit operator some understanding of those risks and possible ways to mitigate them. An accurate, robust simulation tool can assist in this process. For this particular study, ProMax® with TSWEET® and PROSIM® was used, a simulator whose accuracy has been well established in industry. [2][3][4]

## **5C (10F) Temperature Approach Rule**

During operation and design of amine contactors, it has been advised for some time to maintain a minimum temperature approach of 5C (10F). The temperature approach is defined as the temperature differential between the incoming acid gas and the lean amine feed. The reason for this guideline is to prevent the condensation of hydrocarbons in the contactor and avoid the subsequent problems that a second liquid phase causes an amine plant. [1]

However, it is well known that for most cases decreasing the temperature of the absorber can increase its performance. This is especially true for primary and secondary amines with little kinetic involvement. Even for MDEA there are potential performance gains for the absorption of H<sub>2</sub>S, whose kinetics are quite fast, at the expense of CO<sub>2</sub> whose absorption would be lowered due to the temperature effect on the kinetic rate. [5] Many times it is impractical or undesirable to lower the absorber temperatures by cooling the sour gas feed, so one option is to lower the temperature of the

lean amine as much as possible. However, this could require violating the 5C (10F) approach rule of thumb.

While the potential gains from cooling the absorber are obvious, the possible detrimental effects are equally as obvious. Liquid hydrocarbons can create many problems in the amine plant itself, such as foaming, shortening the life of carbon filters, and loss of product.[6][7][8] Increased hydrocarbons in the amine solution can also be problematic for downstream units such as Claus plants.

The question for the designer or operator is then, when does a hydrocarbon phase form, if at all? Also, while the absorption of H<sub>2</sub>S is increased with lowering temperature, so too is the absorption of hydrocarbons. Does the good outweigh the bad?

To study these questions, four representative streams were selected from various locations in Central/Eastern Europe. These gases, shown in Table 1, are from various sources, operate at various pressures, and have quite different compositions and hydrocarbon dew points.

	Russia	Hungary	Czech	Kazakh
<b>DewPoint</b>	(10 C)	5 C	15 C	25 C
<b>Pressure</b>	2.7 bar	25 bar	3 bar	25 bar
<b>H<sub>2</sub>S</b>	0.5	0	2.2	26.5
<b>CO<sub>2</sub></b>	1.2	19.5	0	3.5
<b>NH<sub>3</sub></b>	0	0	0.89	0
<b>MeSH</b>	0	0	0	0.1
<b>Hydrogen</b>	0	0	81	0
<b>Nitrogen</b>	16	5.61	0	1.2
<b>Methane</b>	38	69.87	7.5	35
<b>Ethane</b>	18.2	2.64	3	17
<b>Propane</b>	16.5	1.17	2.7	12
<b>i-Butane</b>	4.8	0.26	1	1.4
<b>n-Butane</b>	2.3	0.43	1	2.3
<b>i-Pentane</b>	1	0.15	0	0.5
<b>n-Pentane</b>	1	0.14	0	0.35
<b>n-Hexane</b>	0.5	0.14	0	0.15
<b>n-Heptane</b>	0	0.09	0.5	0
<b>n-Octane</b>	0	0	0.2	0
<b>n-Nonane</b>	0	0	0.01	0

Table 1: Feed compositions and conditions

Each of these streams is fed to an amine absorber and the lean amine temperature is varied from 10 to 50C. Two things should be noted. First, all four streams are fed to the absorber at 40C and are saturated with water. Since condensing a non-aqueous phase is of concern, the hydrocarbon dew point is what is most important and is shown in Table 1. Second, some practical limitations for the system must not be ignored. For example, temperatures below 25C for an MDEA solution cause a dramatic increase in the solution viscosity making operation of the contactor exceedingly difficult. However, since most lean amine streams are cooled with aerial coolers, it is rarely practical to reduce

the lean amine temperatures to extremely low temperatures in most climates. These temperatures were selected simply to emphasize the trends.

Of interest are the increased solubility of hydrocarbons in the amine solution, increased performance of the absorber, and the presence of a second liquid phase on any trays. Each of the feeds was treated with a 50% MDEA solution with the exception of the Hungarian gas stream which was treated with a mixture of MDEA and piperazine. The results from this study are presented below:

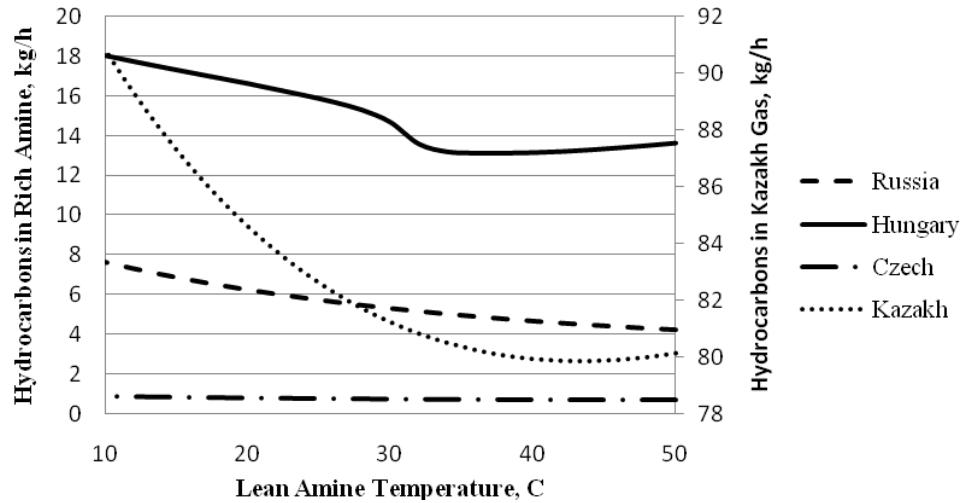


Figure 1: Hydrocarbon increase in rich amine

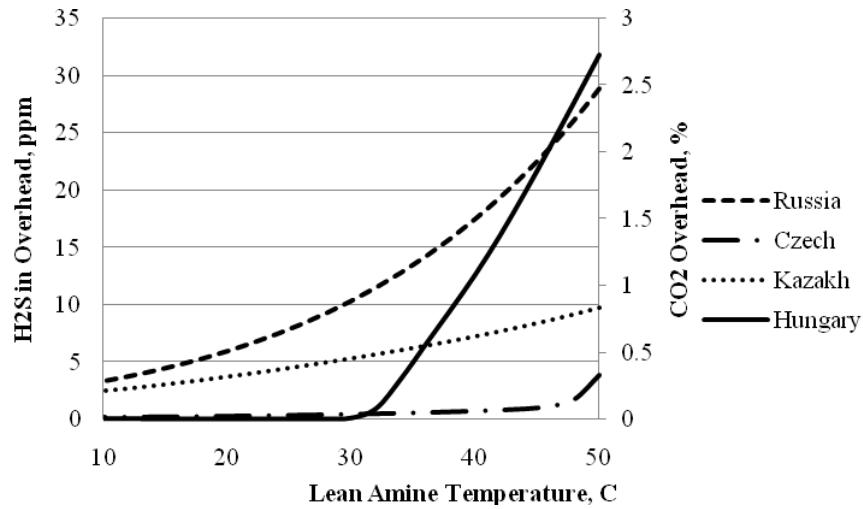


Figure 2: Performance of absorber at varying lean amine feed temperatures.  $\text{H}_2\text{S}$  scale represents only Russian, Czech, and Kazakh gas while the  $\text{CO}_2$  scale represents only the Hungarian gas.

As can be seen, the performance of each of these absorbers is increased considerably by reducing the trim cooler temperature. The general rule of thumb would require a lean amine temperature of 45C.

However, violating this rule and reducing the lean amine temperature to 35C—if possible—produces absorber performance gains from 60 to 150%. These performance gains are offset by an increased hydrocarbon pick from -5 to 15%. The acid gas absorption curves are quite steep while the hydrocarbon curves are not in most cases.

One point of interest for the Hungarian gas is the inflection point in the hydrocarbon solubility curve. This inflection point matches exactly with near complete absorption of CO<sub>2</sub> in the feed gas. It has been established that an increase in loading for an amine solution reduces the solubility of hydrocarbons in the liquid. Once the bulk of the CO<sub>2</sub> has been removed and the rich loading becomes fairly constant, the hydrocarbon solubility begins its expected upward trend as temperature is reduced.

In looking further at the Hungarian gas, whose feed contains no H<sub>2</sub>S at all and a large proportion of CO<sub>2</sub>, some deviation from previous studies is evident. [5] Further investigation showed that high tray temperatures in the bottom of the column minimized any reduction in the kinetic rate for CO<sub>2</sub> absorption. Due to heats of reaction, bottom tray temperatures were raised 30-40C above the gas feed temperatures, creating near equilibrium conditions. The top section of the absorber was mostly polishing the gas since the bulk of the CO<sub>2</sub> had already been removed.

If the CO<sub>2</sub> concentration of the Hungarian gas is reduced from 20% to 2%, trends are seen that agree more closely with those presented by Lunsford and Bullin, as evidenced in Figure 3 and 4.[5] In this case CO<sub>2</sub> absorption is actually lowered by a reduction in absorber temperatures even with the additive piperazine.

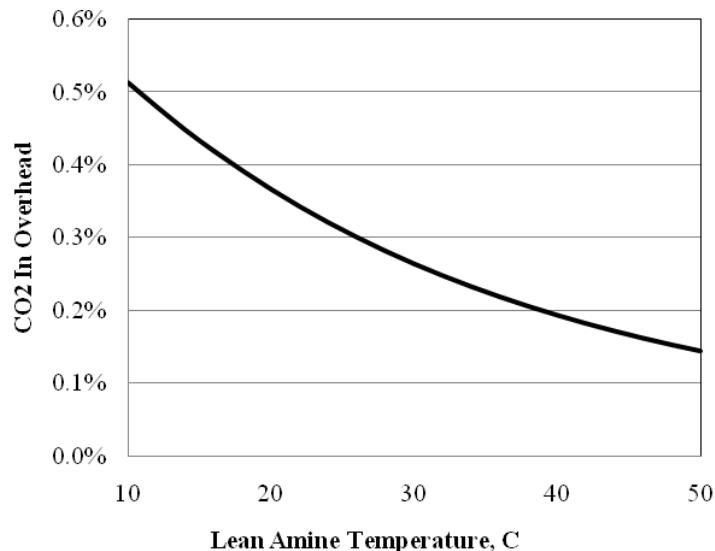


Figure 3: Contactor performance with 2% CO<sub>2</sub> in the Hungary gas

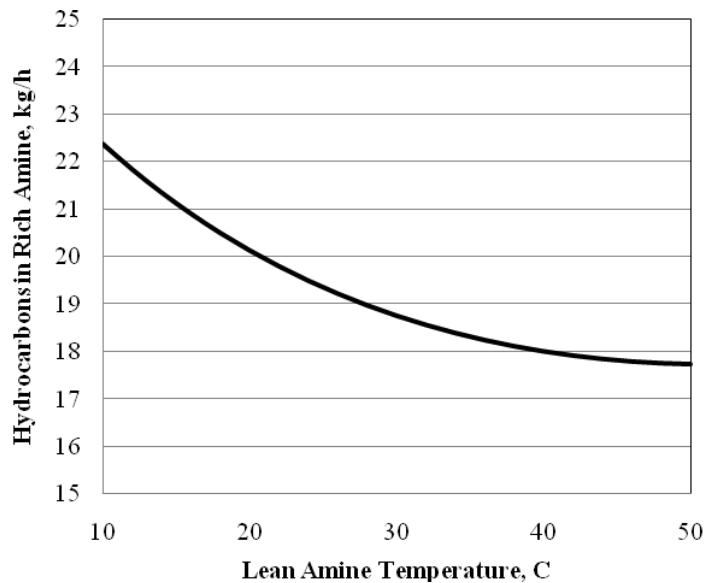


Figure 4: Hydrocarbon Increase with 2% CO<sub>2</sub> in the Hungary gas

The inflection point in the hydrocarbon pick up is also absent from Figure 4 as the solution loading remains fairly constant over the range of lean amine feed temperatures.

In all cases, the formation of a second liquid phase was far below rule of thumb lean amine feed temperatures. The simulator performs a check for a second liquid phase in each piece of equipment throughout the simulation and issues a warning if one is found. In this study the phase threshold, or the amount of a second liquid phase which must be present to constitute a separate phase, was ratcheted down to 0.001% by moles, a level where it is unlikely that the liquid phases would even separate. Temperatures down to 10C showed no warnings issued and there was no formation of a second liquid phase for the Russian, Czech, and Hungarian gases. The only system that formed a second liquid phase was the Kazakh gas, and even here the phase formed at a feed temperature of 28C, which is 17C below the guideline feed temperature of 45C.

	Russia	Hungary	Czech	Kazakh
<b>Feed Temp</b>	40C	40C	40C	40C
<b>Rule of Thumb</b>	45C	45C	45C	45C
<b>Dew Point</b>	-10C	5C	15C	25C
<b>2<sup>nd</sup> Liquid Phase</b>	n/a	n/a	n/a	28C

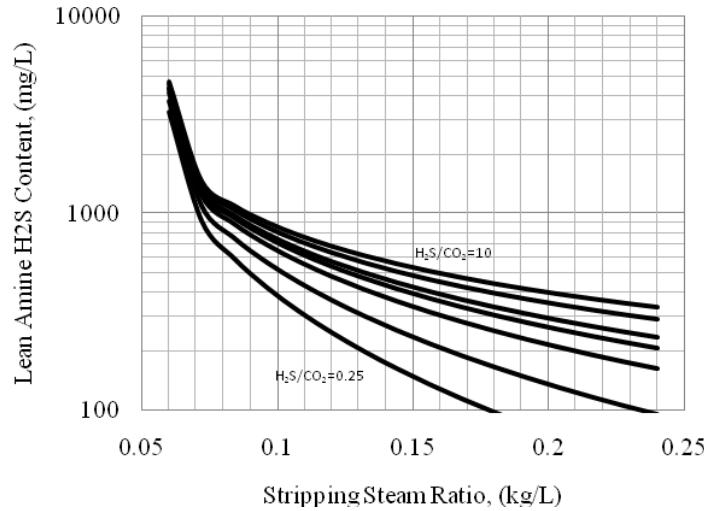
Table 2: Formation of second liquid phase in contactor

In light of this study it would seem that designers and operators should be more concerned with their approach to the hydrocarbon dew point than to the feed gas temperature. For practical purposes it is quite easy to create a temperature control based on the measured feed gas temperature (the hydrocarbon dew point must be calculated and will change with gas composition). However, a blanket rule using the feed temperature set point could cause the designer/operator to miss out on some definite benefits of reducing the trim cooler temperature. Not only is there a potential for

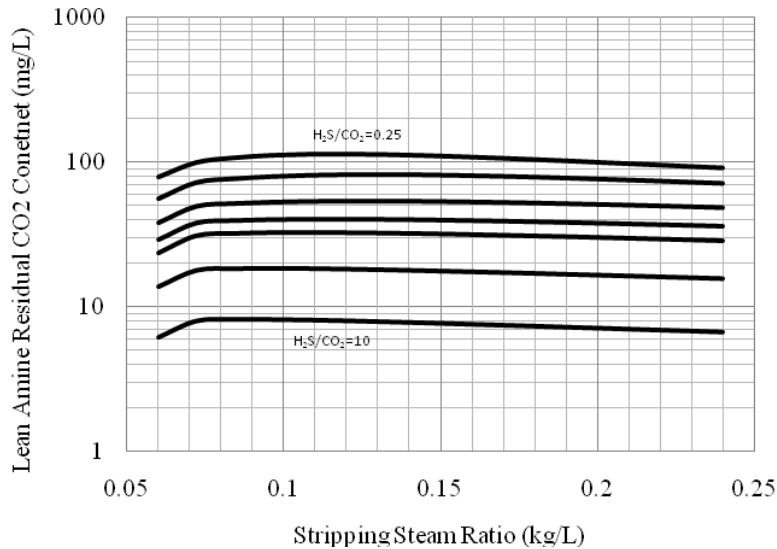
operating cost savings, but the increased performance of the absorber could benefit plants whose feed gas temperature increase, for whatever reason, or whose absorber capacity is becoming limited. As was mentioned earlier, every situation is different. A thorough investigation with the best data available should be performed to assess the benefits and risks of varying the lean amine temperature.

## 0.12 kg/l Steam Rate Rule

In the design and operation of amine strippers, a steam ratio, defined as the mass flow of steam per volume of amine circulation, has been recommended by a variety of sources. [6] The majority of these sources list 0.12 kg/l (1 lb/gal) as an ideal set point for most cases and this ratio has been used in plant operation for many years. But the selection of a proper steam ratio is not as simple as a one-size-fits-all set point. For mixed acid gas cases, the steam ratio plays a major role not only in the quality of the lean amine, but also in its composition. Fitzgerald and Richardson describe how the stripping of H<sub>2</sub>S is aided by the presence of CO<sub>2</sub> in the amine solution. [9] In their study they show that the residual H<sub>2</sub>S in the lean solution is a function of steam stripping rate as well as the H<sub>2</sub>S/CO<sub>2</sub> ratio in the feed gas. These claims are supported both in theory as well as plant operating data for MEA systems. As many present day designs utilize MDEA, and many plants emphasize the removal of H<sub>2</sub>S in lieu of CO<sub>2</sub>, the steam ratio becomes more of a concern. Figure 5 shows the simulator outputs for a system similar to that presented by Fitzgerald and Richardson but for MDEA.



*Figure 5: Residual H<sub>2</sub>S for an MDEA System at feed gas H<sub>2</sub>S/CO<sub>2</sub> ratios of 0.25, 0.5, 1, 1.5, 2, 4, and 10*



*Figure 6: Residual H<sub>2</sub>S for an MDEA system at feed gas H<sub>2</sub>S/CO<sub>2</sub> ratios of 0.25, 0.5, 1, 1.5, 2, 4, and 10*

It can be seen that the selected steam ratio has a considerable effect on the residual H<sub>2</sub>S content in an MDEA solution, especially up to ratios of about 0.07 kg/l (0.6 lb/gal). The costripping effects of CO<sub>2</sub> can also be seen. Meanwhile, the residual CO<sub>2</sub> in the lean solution remains relatively flat as a function of steam ratio.

In this study, the concern is with overall plant efficiency. As the steam ratio changes, so does the quality of the lean amine. Changes to the quality of the lean amine could have several benefits, including a potential change in the total circulation rate which would have a direct impact on the total reboiler duty.

Figures 5 and 6 show that the lean quality of H<sub>2</sub>S is far more dependent on the steam ratio than CO<sub>2</sub>. This also means that the driving force at the top of the absorber, in terms of lean approach for H<sub>2</sub>S, is also highly dependent on the steam ratio. Since many MDEA plants operate with an emphasis on H<sub>2</sub>S removal alone, it is more appropriate to determine the required circulation rate in terms of H<sub>2</sub>S overhead specification and allow the CO<sub>2</sub> overhead to be what it may.

To test the efficacy of the 0.12 kg/l steam ratio, a case study was set up varying the steam ratio from 0.06-0.18 kg/l (0.5-2 lb/gal) and the circulation rate set to the minimum required to achieve the desired overhead H<sub>2</sub>S composition. The results from this study are presented in Figure 7. The study was done for feed streams with three different H<sub>2</sub>S/CO<sub>2</sub> ratios and a constant absorber pressure of 25bar.

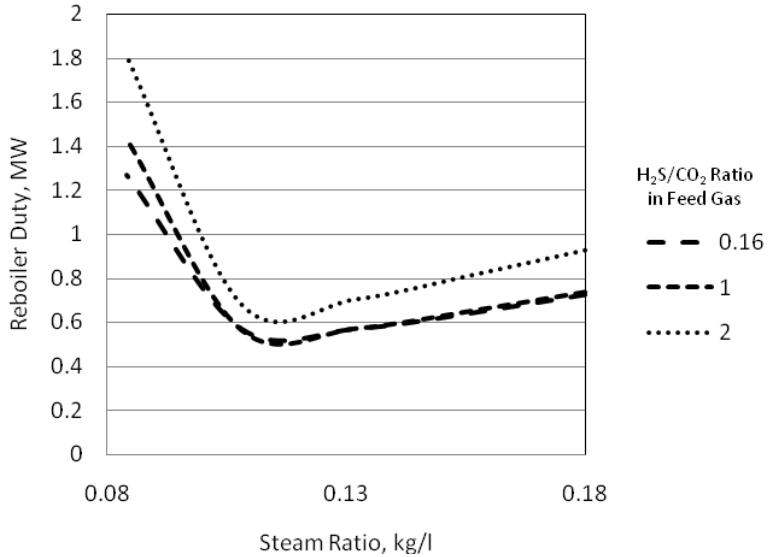


Figure 7: Effect of Steam Stripping Rate on Total Reboiler Duty

It is clear that for all three cases, while the rule of thumb steam rate is adequate, there is room for improvement. Each case showed a minimum total reboiler duty, and subsequently circulation rate, at around 0.09-0.1 kg/l. This is a ratio that is over 15% lower than the rule of thumb. The results are total reboiler duty reductions from 10-15%.

Again, every case is different and requires a thorough investigation. While a blanket rule of thumb is an adequate starting point, it does not always result in an optimized design.

## Lean Rich Outlet Temperature

A rule of thumb that many designers and operators have been interested in ignoring, at least in the authors' experience, is the outlet temperature on the rich side of the lean/rich exchanger. A set point of 99C (210F) has been well established over the years in both operation and the literature with only minor variations. [1][6] In fact, one source even claims that setting an outlet temperature higher than 104C provides no additional benefits to the overall process. [6] This seems counter-intuitive to many engineers who wish to increase heat integration in their plant to as high a level as possible.

Besides the effect on stripping the amine, acid gas breakout at high rich amine temperatures is also of concern. If a large amount of gas breakout is present, erosion/corrosion can occur both in the exchanger as well as the process lines to the stripper. [10] 99C (210F) is a generally accepted maximum temperature to avoid acid gas breakout and corrosion problems in the equipment. [1][10][11]

To test whether there are benefits to increasing this temperature, a case study was performed for an MDEA system. The rich side temperature was varied from 70C-120C and, to see any benefits to the stripping of the acid gas, a lean quality was set and the reboiler duty was allowed to float. Special attention was paid to the amount of vapor that was generated in the rich amine as well as the

composition of acid gas in this vapor. It should be pointed out that practical limitations in terms of temperature approaches in the lean/rich exchanger were generally ignored.

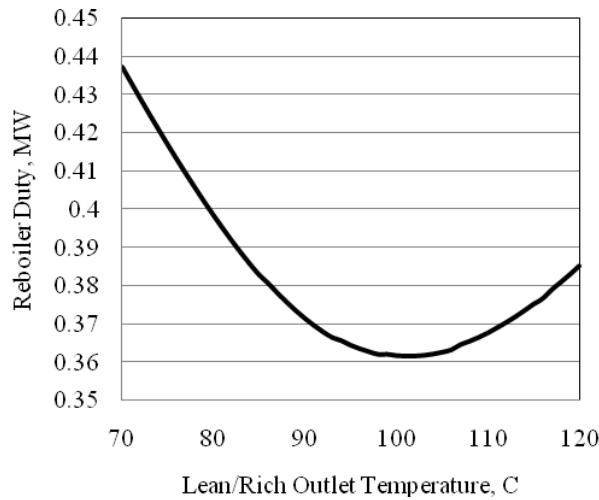


Figure 8: Rich amine outlet temperature effect on total reboiler duty

Figure 8 shows the total reboiler duty for an MDEA solution with a rich loading of 0.3 mol/mol. This graph seems to completely support the 99C set point as this temperature is the minimum for the process. However, this does not tell the complete story. Figure 9 shows that the minimum is not at a constant temperature but rather seems to be a function of loading varying by 5-10C. Figure 10 shows the results more clearly; as the rich loading increases so too does the benefit of increasing the lean/rich outlet temperature. As much as a 5% reduction in reboiler duty can be achieved.

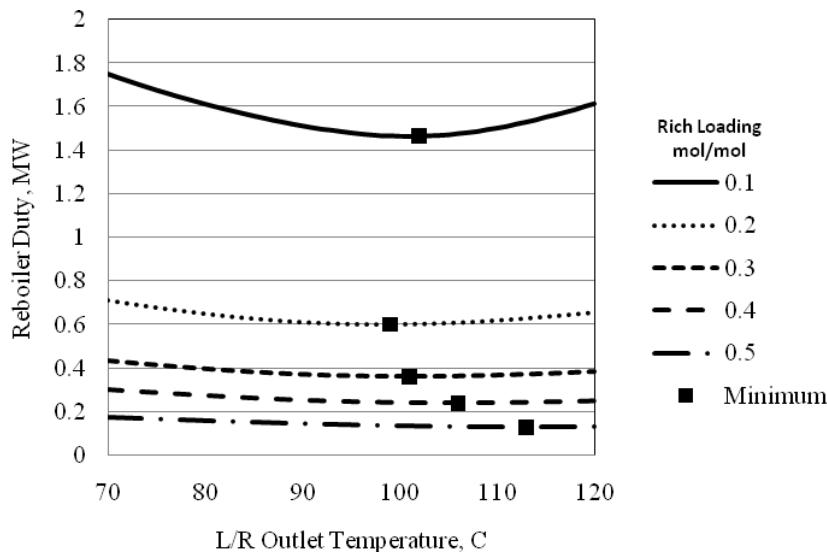
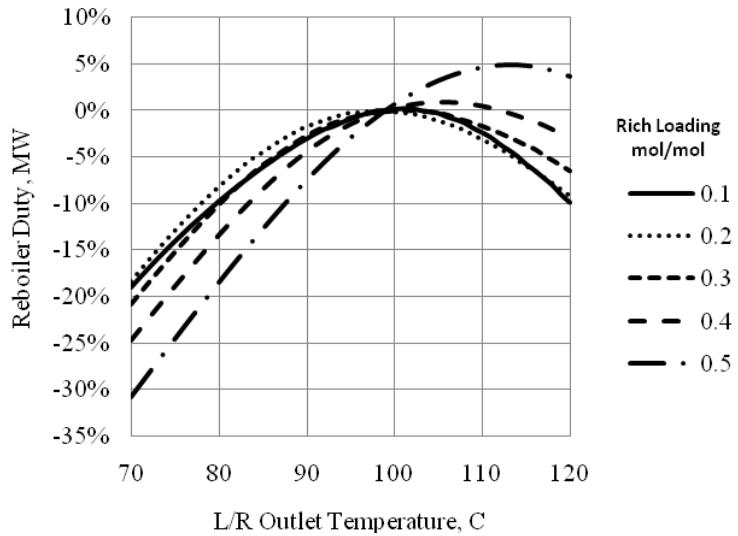
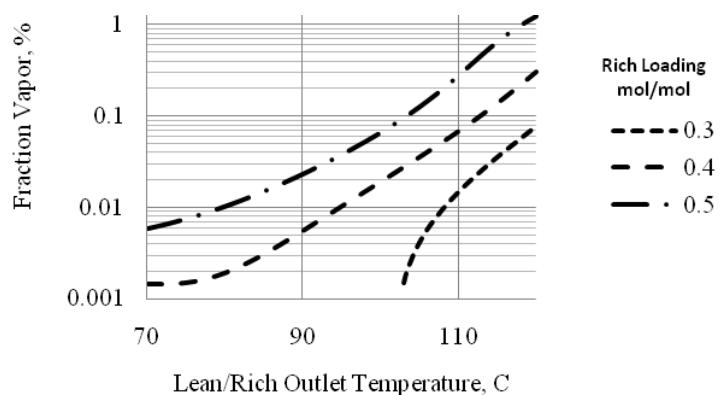


Figure 9: Effect of lean loading on lean rich outlet temperature optimum

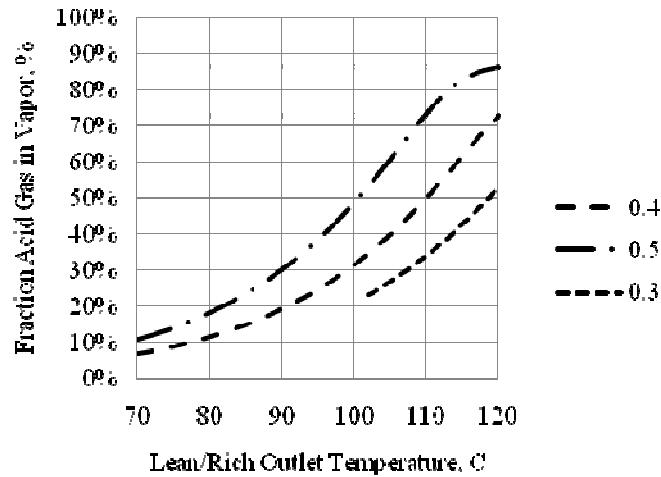


*Figure 10: Effect of lean loading on lean rich temperature optimum as compared to 99C*

The question of acid gas break-out remains, although many designs today utilize metallurgy in this area of the plant to mitigate this concern, the amount of vapor and the acid gas composition both increase with rising temperature as do corrosive effects. Regardless, the systems loaded to 0.4 mol/mol showed the presence of some acid gas breakout at lean/rich outlet temperatures as low as 70C.



*Figure 11: Acid gas breakout in lean/rich exchanger*



*Figure 12: Fraction of the vapor phase comprised of acid gas*

Once again, each situation is different. In the case of this study the 99C set point worked well for many loadings, but for higher loadings there was some room for improvement. An investigation into the acid gas break-out risks, weighed against potential benefits to the reboiler, should be conducted on a case-by-case basis.

## Regenerator Pressure Rule

It is generally recommended to operate amine regenerators at approximately 2.1-2.2bar. [1][6] Typically, stripping is conducted at low pressure and high temperature, but for amine strippers, where the bottoms composition is nearly constant, the reboiler temperature is tied directly to the reboiler pressure. Elevating the regenerator pressure as a means to increase stripping is then proposed. [6] However, there is a limit to the extent to which the temperature can be raised as a result of thermal degradation of the amine. [11][12] Pressures where the reboiler temperature is high but does not exceed 127C are therefore typically used [6].

It has often been pointed out that the normal bulk temperature in the reboiler is well below the degradation temperature. This makes perfect sense for direct fired reboilers which may experience high skin temperatures. However, when the heating medium is steam, the skin temperature is often much closer to the bulk temperature and it may be possible to elevate the reboiler temperature further without experiencing thermal degradation.

Even though thermal degradation of the amine cannot be modeled in the simulator, the potential benefits of elevating the reboiler pressure above the general rule of thumb can be analyzed. It can then be determined whether the risk of changing this operating point is worthwhile.

To conduct this study, an MDEA regenerator with a constant rich loading was modeled with varying system pressures. The lean quality was set and the reboiler duty was allowed to float. Figure 13 shows that at 5 bar the bulk amine temperature does begin to approach the thermal degradation point of 176C. [11]

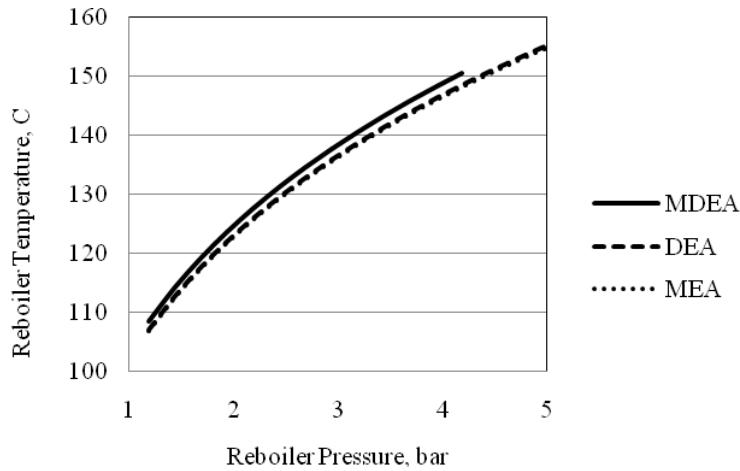


Figure 13: Reboiler temperature at various pressures

In Figure 14 it can be seen that in almost all cases increasing the reboiler pressure, and subsequently temperature, actually reduces the required reboiler duty. It is most evident for MEA and DEA while MDEA shows smaller gains, though still quite large on a percentage basis.

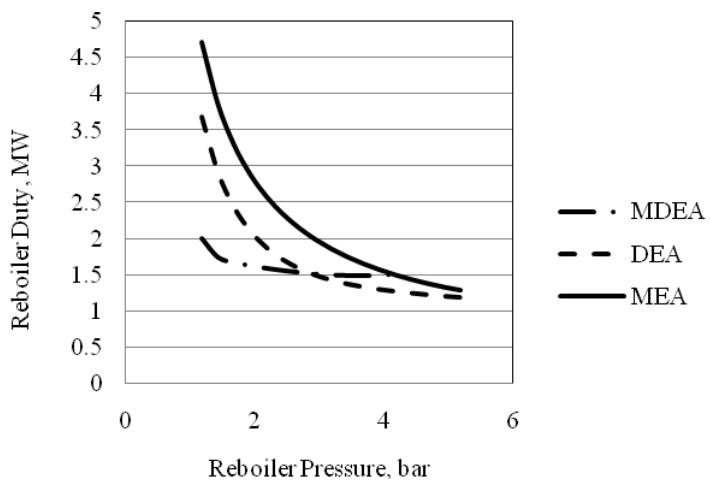


Figure 14: System performance at various reboiler pressures

In splitting up the rich loading between CO<sub>2</sub> and H<sub>2</sub>S, it can be seen that CO<sub>2</sub> is the main benefactor of increasing the reboiler pressure, at least for MEA and DEA. However, MDEA, for the mixed acid gas case, shows a definite minimum at around 3 bar. Meanwhile the only other minimum was for the DEA-CO<sub>2</sub> only case at around 4 bar. Also for MDEA, the CO<sub>2</sub> only case actually exhibited a behavior that was opposite from what was expected. For this particular system, increasing the regenerator pressure actually hurts the performance of the reboiler.

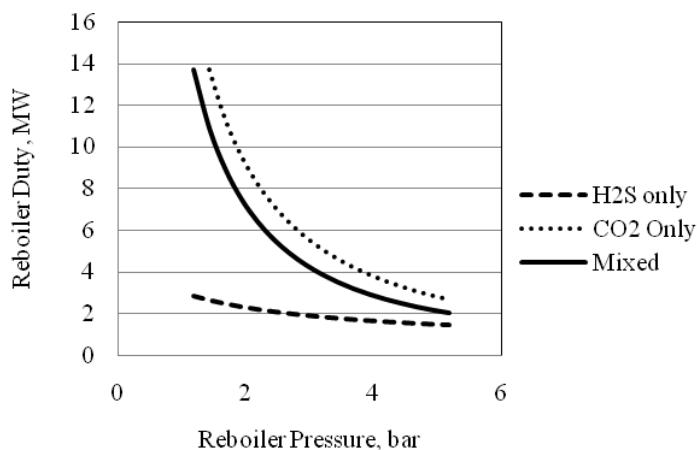


Figure 15: MEA System

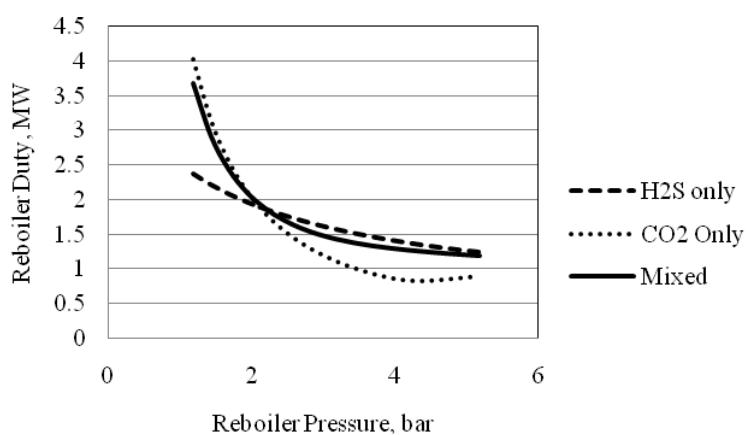


Figure 16: DEA System

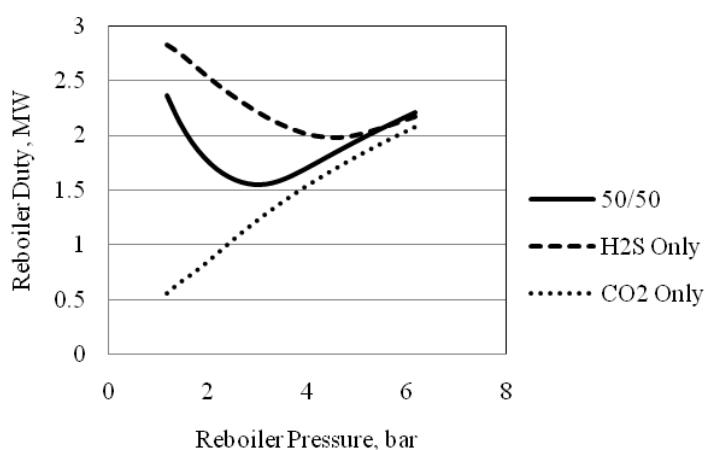
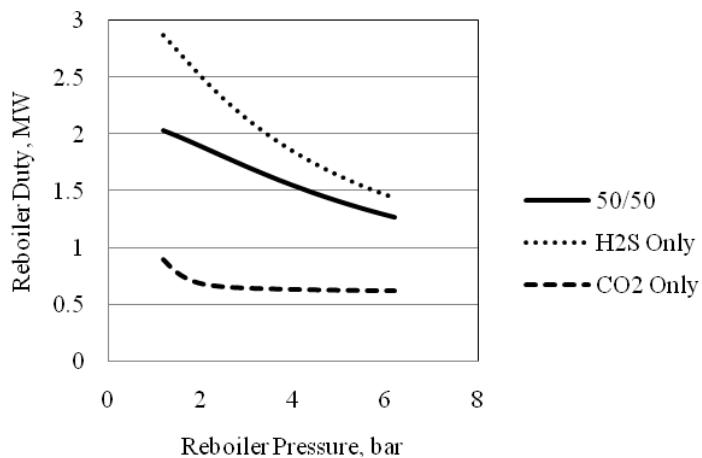


Figure 17: MDEA System

In all of these studies, the temperature of the rich feed to the column was held at a constant 99C. Therefore, higher reboiler temperatures required larger amounts of sensible heat to elevate the amine temperature to reboiler conditions. It is believed that for MDEA, the increased heat requirements are entirely a result of this increase in sensible heat. For the DEA CO<sub>2</sub> only case, these effects only begin at around 3.5-4 bar where the partial pressure of CO<sub>2</sub> begins to level off with respect to temperature.

Figure 18, where the rich feed temperature is allowed to float as a function of reboiler temperature, seems to bear this out. With a sensible heat requirement that is more constant, the MDEA-CO<sub>2</sub> only case behaves similarly to the MEA and DEA cases.



*Figure 18: Reboiler duty for MDEA system with 20C rich amine/reboiler temperature differential*

It would appear that the point where the sensible heat requirements begin to dominate is dependent on the strength of the base. For MEA, the sensible heat effects are never seen, while for DEA they begin at 3.5 to 4 bar and for MDEA the effects are immediately apparent. As a check a fourth case was examined for TEA, a tertiary amine. TEA exhibited similar behavior to MDEA.

So it seems that increasing the reboiler pressure could provide some benefits, though it depends on the system. The benefits also depend very much on the rich feed temperature and the amount of sensible heat required to elevate the amine to reboiler temperature.

## System Comparison

To see the potential benefits of changing set points away from the various rules of thumb previously discussed, a comparison was undertaken for two identical MDEA units. The first unit is modeled using all of the standard guidelines as currently held in the literature. The second model is based on optimal set points which violate some rules of thumb. Table 3 shows the primary differences.

		<b>Standard</b>	<b>Modified</b>
<b>Lean Amine Temp</b>	C	45	35
<b>Steam Ratio</b>	kg/l	0.12	0.1
<b>Lean/Rich Temp</b>	C	99	116
<b>Reboiler Pressure</b>	bar	2.14	3

*Table 3: Input variations between standard and modified MDEA system*

Table 4 shows the results of this comparison. As is evident, considerable performance gains can be obtained by changing the set points for this particular unit. The 28% reduction in reboiler duty can either be seen as an operating cost reduction or as a means to increase unit throughput. Not only was the reboiler duty reduced, but the circulation rate was also reduced by approximately 15%. This allows for smaller equipment, lower capital costs or higher throughput in existing equipment. Only small changes away from the rules of thumb were required to achieve positive results.

<b>Feed Gas</b>		<b>Standard</b>	<b>Modified</b>
<b>H<sub>2</sub>S</b>	%	0.5	0.5
<b>CO<sub>2</sub></b>	%	3	3
<b>Flow</b>	Nm <sup>3</sup> /h	50000	50000
<b>Overhead</b>			
<b>H<sub>2</sub>S</b>	ppm	30	30
<b>CO<sub>2</sub></b>	%	1.93	2.09
<b>Lean Amine</b>			
<b>Rate</b>	Sm <sup>3</sup> /h	32.7	28.1
<b>Duty</b>			
<b>Reboiler</b>	MW	2.33	1.67
<b>Condenser</b>	MW	0.79	0.51
<b>Trim Cooler</b>	MW	1.17	1.19
<b>Pump</b>	kW	33.61	27.68

*Table 4: Comparison of standard rules of thumb and modified MDEA system*

## Summary and Conclusions

A recurring theme in this work is that there are no rules of thumb which always apply; every situation is different. Many rules of thumb are presented in the literature and most of them are based on established criterion and work. However, just because they work in most situations does not mean they are always the best choice. The four rules evaluated in this study all showed some flexibility and potential benefits if modified slightly. They each should be considered as a starting point, a first guess. A thorough evaluation should be performed to optimize performance and minimize costs. The benefits of deviating from these guidelines should be weighed against the risks.

## Acknowledgements

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