

Extraction Unit Sulfolane Solvent Regeneration

by

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Abstract

Aromatics extraction units employ a solvent to separate Aromatic compounds from other hydrocarbons. Sulfolane is one common compound used in the closed solvent loop process. Over time the solvent fouls, harming operation. Online solvent regeneration is performed to mitigate the deleterious effects of degradation.

Solvent regeneration is fraught with difficulties stemming from Sulfolane's physical properties and from the nature of cleansing nasty impurities from an uncooperative solvent. Here we examine the operating and design issues associated with the three prevalent types of solvent regenerators: Steam Assisted, Reboiled, and Flash.

Introduction

Liquid-Liquid extraction units don't wear their solvent out as it circles round the unit, but the solvent does deteriorate and becomes fouled, harming operation and contributing to corrosion. Aromatics Extraction (Figure 1) units using Sulfolane as a solvent suffer from solvent contamination and address this problem by online solvent regeneration.

Solvent regeneration is fraught with difficulties stemming from Sulfolane's physical properties and from the nature of cleansing nasty impurities from an uncooperative solvent. Here we examine the operating and design issues associated with the three prevalent types of solvent regenerators.

Solvent Degradation

Reported Sulfolane (Figure 2) decomposition temperatures are 392 °F [1] and 516 °F [2]. The literature suggests 392 °F is the onset of decomposition, while the high decomposition rate at 516 °F is easily observed. Oxygen's presence accelerates decomposition [1, 3, 4]. Unacceptably high corrosion at Paraffin Stripper and Aromatics Stripper reboiler temperatures of 350 °F to 380 °F can be experienced in units with oxygen intrusion. The reboilers and their associated equipment are corrosion focal points [3].

Solvent degradation products include SO₂, acids and polymers [1, 5]. Acids are by their nature destructive. Many polymers are miscible in Sulfolane [6, 7]. Those that stay in solution reduce solvent power, those that do not foul equipment.

Sulfolane is also a good solvent for capturing acid gases and Mercaptans. It is part of the solvent system employed in an acid gas sweetening process. Any acid gas evolving from Sulfolane decomposition or associated corrosion could be held in solution throughout at least part of the extraction unit interacting with degradation products and accelerating corrosion.

Corrosion resulting from degradation contributes byproducts to the solvent flow including; Iron solids, acid salts, and polymer solids. These accumulating wastes accelerate corrosion through erosion/corrosion, foul equipment, and lessen solvent power. These materials cannot escape the solvent loop as they are bottomed with Sulfolane from each column they enter.

The solvent decomposition mechanism is temperature related. Minimizing reboiler heat medium temperatures reduces decomposition and corrosion. Although bulk reboiler temperatures may be below the decomposition temperature, film temperatures are higher. Some units employ fired heater reboilers that accelerate decomposition with their high film temperatures. Regenerators should operate at as low a temperature as possible. This leads directly to low operating pressures to accommodate Sulfolane's low vapor pressure.

Electrolysis studies provide some decomposition mechanism information. Upon electro-oxidation [8], Sulfolane decomposition products include: CO₂, SO₂, Butene and Butane. Butene formation suggests a straightforward polymer production route. Butane formation reveals the importance of Hydrogen donors (acid, Water) in that Sulfolane possesses only 8 Hydrogen atoms while Butane has 10. Without Hydrogen donors, it is possible that Butene formation is favored leading to polymer generation.

Regeneration

Solvent regeneration removes heavy material evolving from solvent decomposition and the accompanying unit corrosion. Feed impurities such as chlorides can also be removed by regeneration. Solvent contaminants lower solvent power, foul equipment, and increase corrosion. Almost all extraction unit Sulfolane regeneration is accomplished by vacuum stripping or fractionating a lean solvent slipstream taken from the Aromatics Stripper bottoms [1, 4, 5, 11, 12]. Regeneration is often semi-batch in that the regenerator is periodically shutdown for cleanout. Figure 3 depicts

regeneration in block diagram format. Steam, if any is used, is not included in the figure. Regenerator charge rates are typically between three and 15 gpm. The overwhelming majority of material fed to the regenerator is sent overhead such that it is difficult to think of them as strippers though that is often what they are called.

Clean Sulfolane is taken overhead and returned to the bottom of the Aromatics Stripper as a vapor, or returned to the lean solvent feeding the extractor after being condensed. Particulates, polymers, tars, and acid salts are left behind after the Sulfolane is vaporized in the regenerator. The regenerator bottoms is heavy waste that is typically withdrawn intermittently since its flow rate is very low. Some regenerator vessels are designed with a bottoms volume large enough to permit accumulation of this waste.

Sulfolane vaporization is complicated by its physical properties. The low vapor pressure that makes Sulfolane a good extraction solvent raises regeneration temperatures to near decomposition values, and certainly to a range at which corrosion is known to occur in other areas of the unit. Additionally, Sulfolane freezes at a high temperature, making the recovery of regenerated solvent more difficult if it must be condensed (though the freeze point declines with increasing Water content). The solids-bearing regenerator residue freezes at a temperature higher than Sulfolane, complicating regenerator bottoms handling.

Table 1 details Sulfolane's properties. Figure 4 depicts Sulfolane's vapor pressure by plotting Equation 1 [6] and individual data points [1, 2, 7].

$$\text{Vapor Pressure (psia)} = 0.145038 \times 10^{[27.8073 - 4350.7/T(K) - 6.5633 \times \log_{10}(T(K))]} \quad (\text{Eqn 1})$$

Lean solvent from the Aromatics Stripper bottoms contains a small amount of Water, typically 0.3 to 0.5 wt percent though it can be higher. This significantly boosts the vapor pressure above that of pure Sulfolane as shown in Figure 5. However, lean solvent vapor pressure without Water present may actually be lower than that of pure

Sulfolane due to the presence of heavies. Once in the regenerator, the low lean solvent Water content is quickly driven off. The vaporizing temperature of the Sulfolane and heavies left behind climbs.

Three types of regenerators are commonly employed:

- Steam-assisted
- Reboiled
- Flash

Steam-Assisted Regenerator

To reduce the regeneration temperature, or to operate at the same temperature but at higher pressure, Steam can be used to lower the Sulfolane partial pressure (Figure 6). Lower regen temperatures diminish solvent degradation and corrosion while higher pressures reduce operating costs and shrink equipment size. Steam-assist regenerator operating pressures are usually set so that the regenerator overhead vapor can pressure into the Aromatics Stripper thus eliminating the need for separate vacuum and condensing systems. Many extraction unit discussions describe Steam-assisted regenerators [4, 5, 11, 12]. Steam-assisted Regenerators usually include a reboiler, typically stab-in, to maintain the column temperature that is cooled by vaporization. Stab-in reboilers are troublesome in this service. If they fail due to corrosion they are a lot of work to remove, and they interfere with interior column cleaning and work during turnarounds.

Figure 7 provides estimated operating conditions for a Steam-assisted regenerator. These data assume the use of pure Steam. This is often impractical. Adding fresh Steam increases variable costs. Adding fresh Steam also upsets the unit Water balance. Typically, regenerator Steam is supplied by vaporizing Water collected from unit accumulators and from the Raffinate Water Wash (Figure 1). Collected Water contains some level of Sulfolane. Steam Sulfolane contamination has a large effect on Regenerator operation as seen in Figure 8.

Steam-assisted Regenerator operation and design is also complicated by column internals hydraulics. The Figure 3 material balance illustrates the problem. The column bottoms flow is a very small fraction of the feed. Maintaining effective vapor/liquid contact throughout all trays is difficult with the wide liquid flow range. There is a large risk of blowing flood on the bottom trays. A bubble cap design is likely needed for the bottom trays and their low liquid flow. Picket fence weirs might be another option. Both of these designs, though, will collect particulates in this fouling service where the liquid is known to contain solids. Some regenerators do not use tray outlet weirs for this reason. These designs essentially employ baffle trays. Sieve trays are also preferred versus valve trays in this fouling service.

While Steam-assist regenerators are technically feasible, they are difficult to operate effectively due to the problems discussed above.

Reboiled Regenerator

Without Steam-assist, Sulfolane can be regenerated in a reboiled column (Figure 9), though at a lower pressure. Figure 10 provides estimated reboiled regenerator conditions. The required reboiler duty is similar to that required for the Steam-assist regenerator.

Reboiled regenerators typically have forced reboilers, and employ as low a temperature reboil medium as possible to minimize solvent decomposition. The pumped reboiler is necessary to reliably feed the viscous, polymeric, solids laden regenerator bottoms, and to improve reboiler heat transfer coefficients thus permitting the use of the lowest temperature heat source. The reboiler outlet temperature rises with the bottoms heavies concentration. Waste is withdrawn when reboiler capacity is expended, or when a temperature target is reached.

Because feed vaporization occurs primarily in the reboiler, the tray liquid flow rates across the column are fairly constant easing tray design.

Reboiled regenerator operating pressures are lower than any other part of the extraction unit. They require their own vacuum system. Pressures lower than the Steam-assist design mean comparatively larger equipment. The reboiler feed pump is also added capital compared to the Steam-assist regenerator.

Reboiled regenerators usually condense their overhead to support their vacuum system's operation. Because Sulfolane freezes at ~83 °F, condensing heat exchangers must be designed to maintain higher film temperatures. Recirculated air-coolers should be considered. Tempered Water may also be appropriate. Sulfolane's relatively high viscosity also complicates condensation. Direct contact heat exchange can be employed to obviate many of the condensation problems Sulfolane's physical properties present.

Reboiled regenerators have higher capital requirements when compared to Steam-assist designs, but they are very effective in cleansing the solvent.

Flash Regenerator

There is little or no stripping or rectification taking place in the regenerator. The feed contains a large amount of Sulfolane to be recovered, and a small concentration of heavy, essentially non-volatile impurities. In effect, regeneration is flashing the Sulfolane out of the contaminants; very similar to boiling Salt Water to recover Water while leaving behind a Salt residue. A Flash Regenerator can be employed to clean Sulfolane (Figure 11).

Flash Regenerator operation is similar (temperature, pressure, reboil duty, vacuum, heat exchange issues) to that of reboiled regenerators except that there are no trays. The feed is flashed in two (or more) stages, heated before entering the flash drum and

again in the reboiler. This reduces the temperature the feed is exposed to, and decreases the residence time of the feed at high temperature. Both characteristics diminish solvent degradation.

Flash reboilers eliminate the design and operating problems associated with trays in this service; fouling, corrosion, and L/V variation. Their effectiveness and capital requirements are similar to reboiled regenerators.

Equipment

The difficult and specialized processing associated with solvent regeneration should be supported by complementary equipment design attributes including:

- Vacuum equipment. Steam ejectors can be used to generate vacuum. If rotating equipment is employed, ensure the seal gland has a positive pressure to eliminate oxygen intrusion (double seals are often used).
- Flanges. Utilize minimum 300# flanges in vacuum service to reduce the potential for oxygen intrusion.
- Pumps. Reboiler feed or regenerator bottom pumps should be designed for slurry service. Ensure a positive gland pressure to exclude oxygen (double seals are often used).
- Materials. Stainless steel and duplex stainless resist the corrosive/erosive regenerator environment. Carbon Steel should have augmented corrosion allowances.
- Pipe Velocities. Reboiler feed piping should be sized for slurry service with a 3 - 4 ft/sec velocity to keep solids moving and reduce the potential for erosion. Overhead piping velocities may be very high at 0.5 to 1.5 psia operating pressures.

Other regeneration methods

Other Sulfolane regeneration means are under study or have been employed. These include:

- Packed beds [3]
- Two-stage distillation [13]
- Ion exchange [14]

None of these methods are currently in widespread use.

Summary

Solvent regenerators are complex to design, operate, and maintain. The rewards of effective solvent regeneration are in part unpleasant: a high freeze-point stream of tar and solids. At times it seems the difficult task is not worth the pay-off. But the other rewards are more attractive; higher solvent power, diminished unit fouling, and reduced corrosion. The absence of problems is less tangible than the effort required to overcome the obstacles to effective regenerator operation. Keeping these problems in abeyance, though, contributes greatly to the bottom line in higher yields, lower variable costs, reliable operation, and unit safety. Invest in the needed resources to make solvent regeneration work for you.

Literature Cited

1. **Deal, G. H., et al.**, "A Better Way to Extract Aromatics," *Petroleum Refiner*, **38** (9), pp. 185-192 (September 1959).
2. **Steele, W. V., et al.**, "Vapor Pressure, Heat Capacity, and Density along the Saturation Line, Measurements for Cyclohexanol, 2-Cyclohexen-1-one, 1,2-Dichloropropane, 1,4-Di-tert-butylbenzene, (\pm)-2Ethylhexanoic Acid, 2-(Methylamino)ethanol, Perfluoro-n-heptane, and Sulfolane," *Journal of Chemical Engineering Data* (American Chemical Society), **42** (6), pp. 1021-1036 (1997).
3. "Session IV, Question 30," 1999 NPRA Question & Answer Session on Refining and Petrochemical Technology, National Petrochemical & Refiners Association (2000).
4. **Huggins, R. L.**, "Sulfolane Extraction of Aromatics," AIChE 1977 Spring National Meeting paper.
5. **De Graff, R. R.**, "Aromatic Hydrocarbon Recovery Process," United States Patent 3,466,345.
6. **Riddick, J. A., Bunger, W. B., et al.**, "Organic Solvents Physical Properties and Methods of Purification," 4th Ed., John Wiley & Sons, New York, pages 686, 1110 (1986).
7. **Jordan, T. E., Kipnis, F.**, "Solubility Characteristics of Sulfones," *Industrial and Engineering Chemistry*, **41** (11), pp 2635-2637 (November 1949).
8. **Wasmus, S., Vielstich W.**, "Electro-Oxidation and Reduction of Dimethylsulfoxide and Sulfolane in Aqueous Acid Solution - An On-line MS Study," *Electrochimica Acta*, **38** (2/3), pp. 175-183 (1993).
9. "Shell Sulfolane-W," Technical Bulletin Shell Chemical Company (April 1984).
10. **Yu, Yang-Xin; Liu, Jian-Gang; et al.**, "Isobaric Vapor-Liquid Equilibria and Excess Volumes for the Binary Mixtures Water+Sulfolane, Water+Tetraethylene Glycol, and Benzene+Tetraethylene Glycol," *Journal of Chemical Engineering Data*, **45** (4), pp. 570-574 (2000).
11. **Asselin, G. F.**, "Aromatic Hydrocarbon Separation Via Solvent Extraction," United States Patent 4,058,454.
12. "Aromatics and Derivatives - Suloflane Process," UOP LLC paper 2699C-22 899ADIV (1999).

13. **Yeary, D. L.**, "Low Color, Low Turbidity Sulfolane," United States Patent 5,223,101.
14. **Lal, K. J., et al.**, "Process for the Purification or Regeneration of Contaminated or Spent Process Sulfolane," United States Patent 5,053,137.

Table 1 - Sulfolane Properties [6, 9]	
Technical Name	Tetrahydrothiophene 1-1 dioxide
Formula	C ₄ H ₈ O ₂ S
Molecular Weight	120.171
Normal Boiling Point, °F	549.14 ¹
Freezing Point, °F	83.2 ²
Density, lb/ft ³	
@ 86 °F (30 C)	78.61
@ 95 °F	78.39
@ 122 °F	77.63
@ 302 °F	72.22
Viscosity, cP	
@ 86 °F (30 C)	10.3
@ 212 °F	2.5

Notes:

1. Decomposition begins before reaching this temperature.
2. Slightly lower freezing point reported in air: 81.3 °F [9].

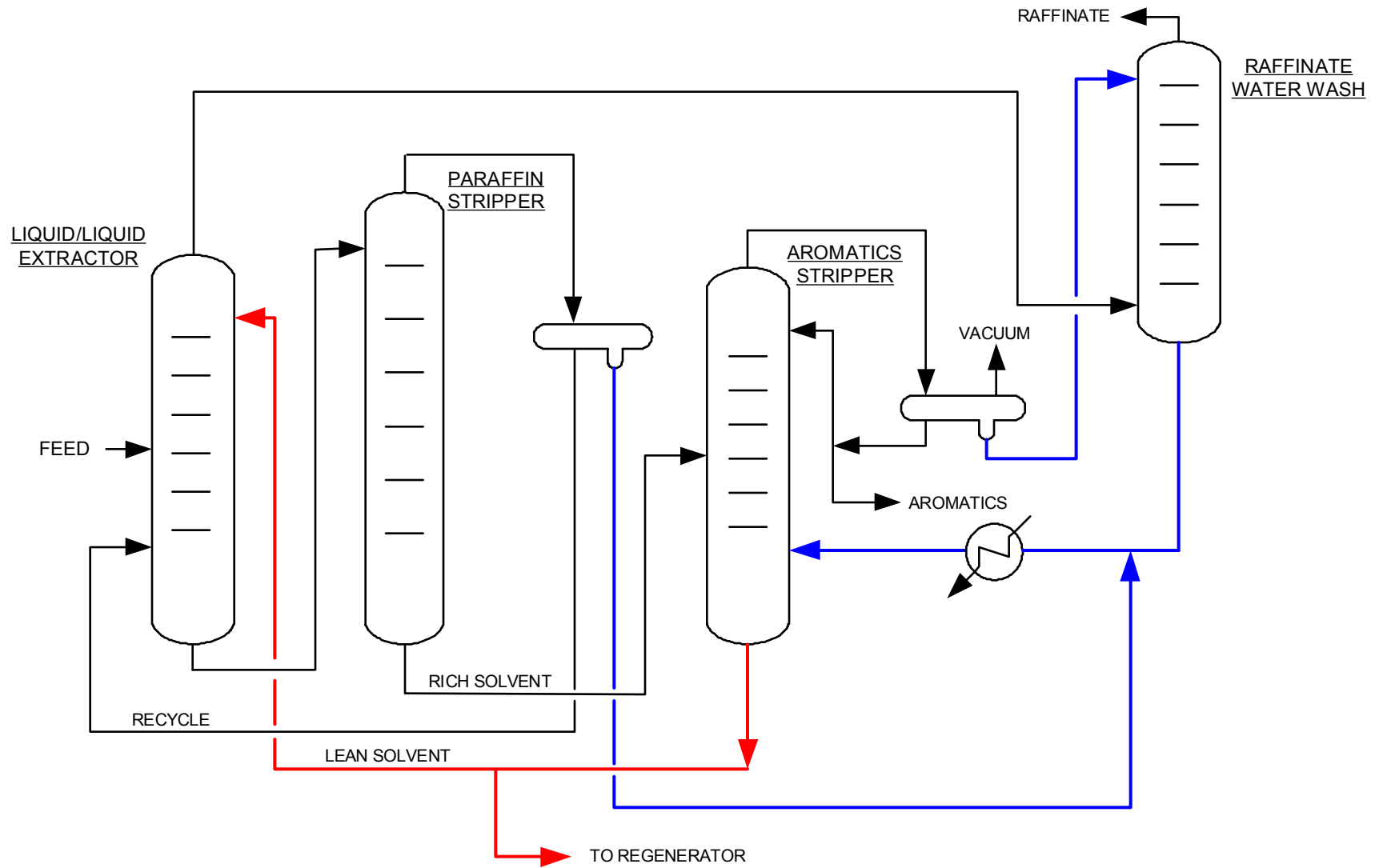
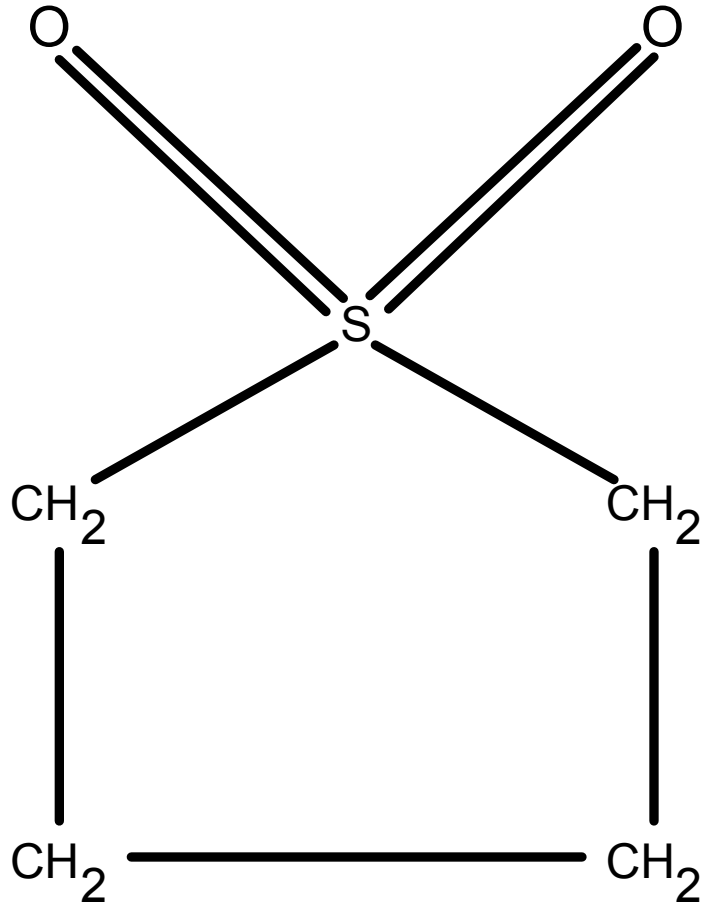


Figure 1 - Aromatics Extraction Unit

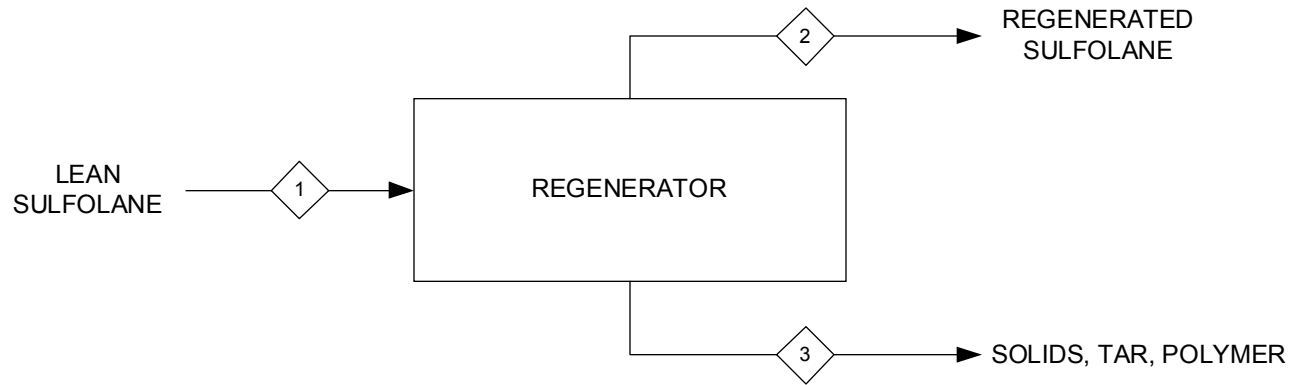
Sulfolane -- Schneider



$C_4H_8SO_2$

Tetrahydrothiophene 1-1 dioxide

Figure 2 - Sulfolane Molecule



STREAM	1	2	3
DESCRIPTION	LEAN SULFOLANE	REGENERATED SULFOLANE	WASTE
WATER, lb/hr	19	19	0
SULFOLANE, lb/hr	6,319	6,116	203
HEAVIES, lb/hr	25	1	24
TOTAL, lb/hr	6,363	6,136	227
GPM	11	10.5	0.5

Figure 3 - Regenerator Block Diagram

Figure 4 - Pure Sulfolane Vapor Pressure

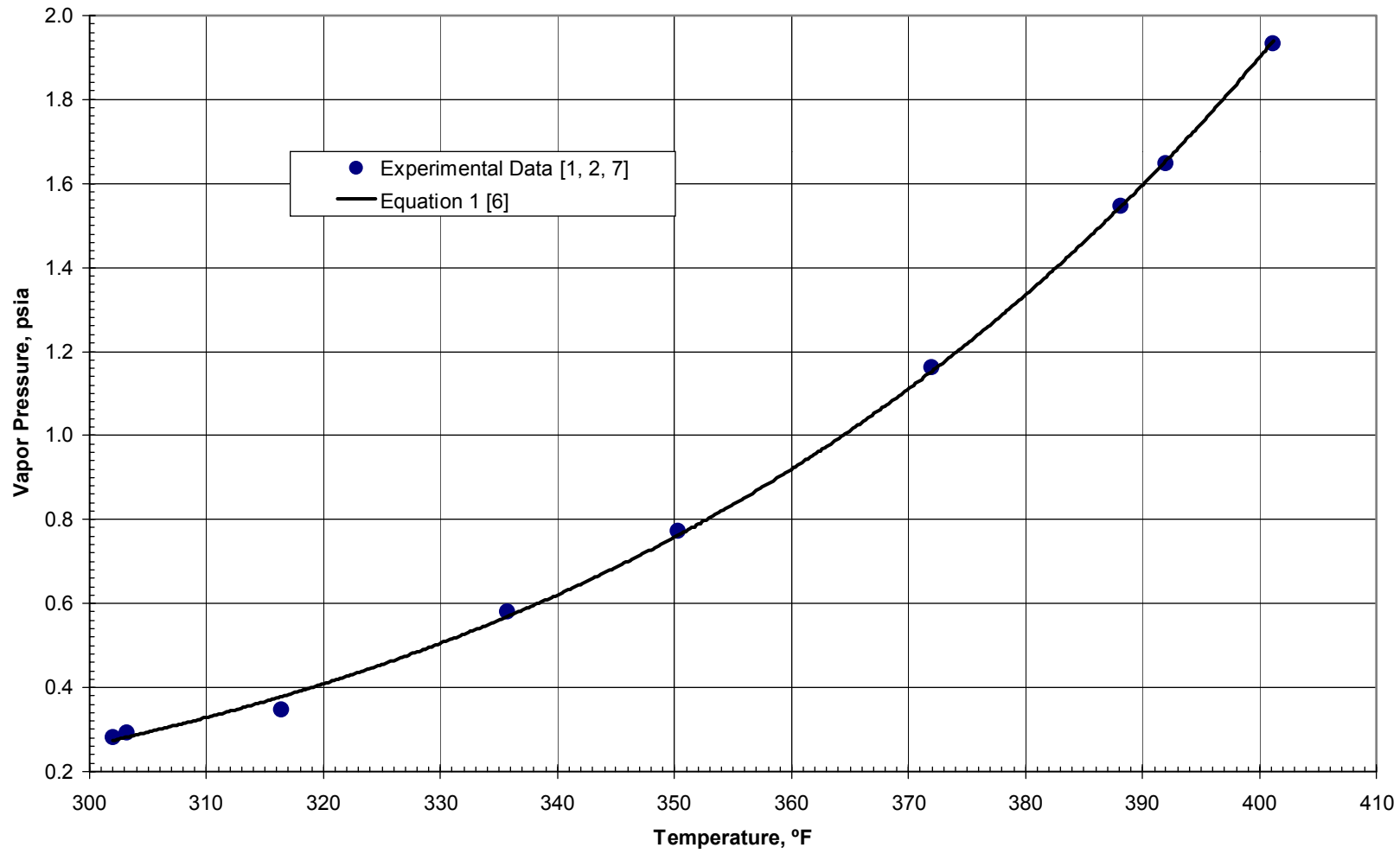


Figure 4

Figure 5 - 0.3% wt Water in Sulfolane Vapor Pressure
NRTL Based [10] Simulation Data

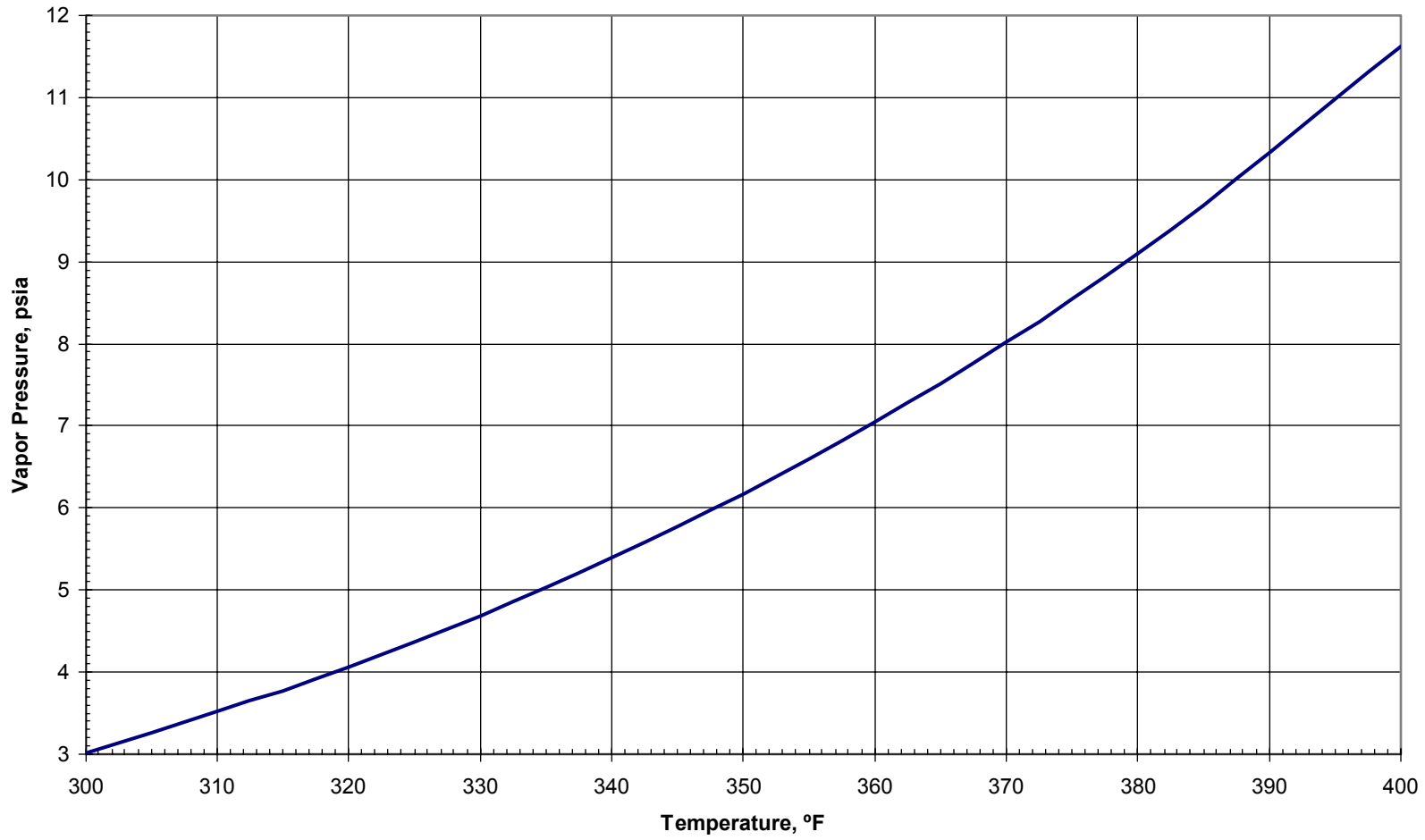


Figure 5

STEAM STRIPPER

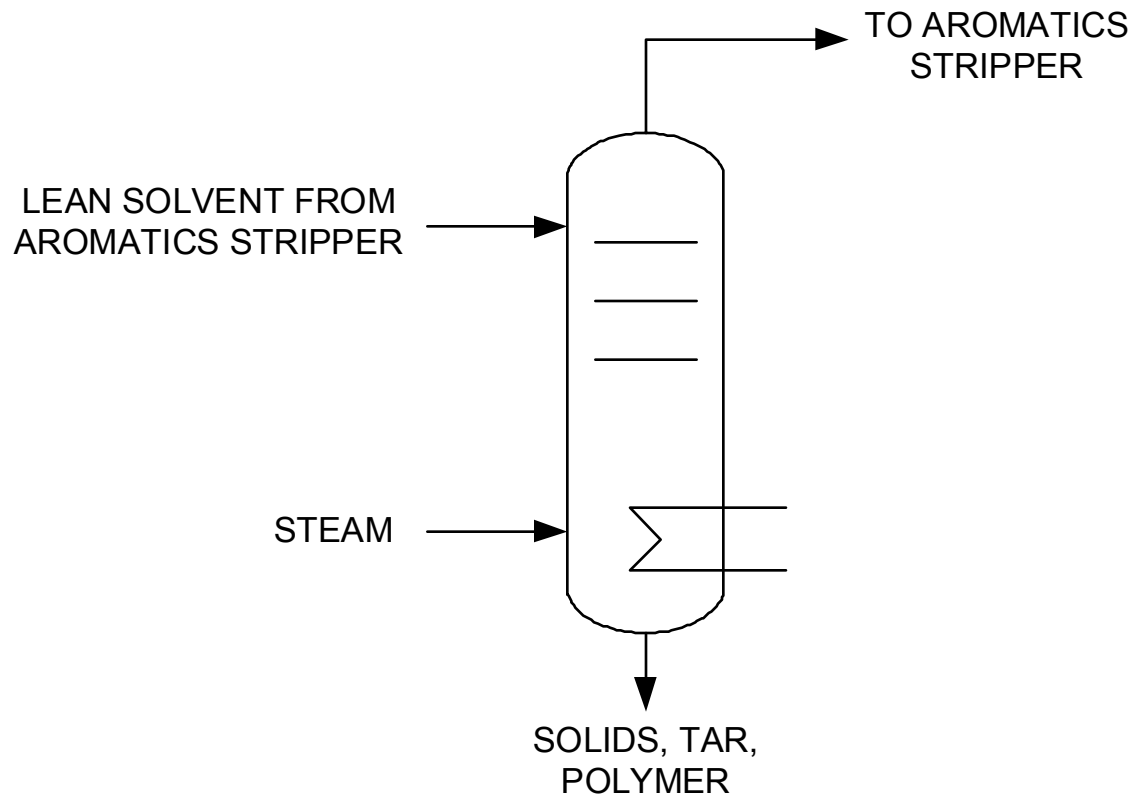


Figure 6 - Steam Assisted Regenerator

Figure 7 - Effect of Operating Pressure on Steam-Assisted Regenerator
NRTL Simulation [10], 11 gpm Regen Feed, 360 °F Feed Temperature, 0.4 wt% Heavies in Feed, Bottoms Temperature held @ 360 °F, 97% of Sulfolane in Feed Recovered

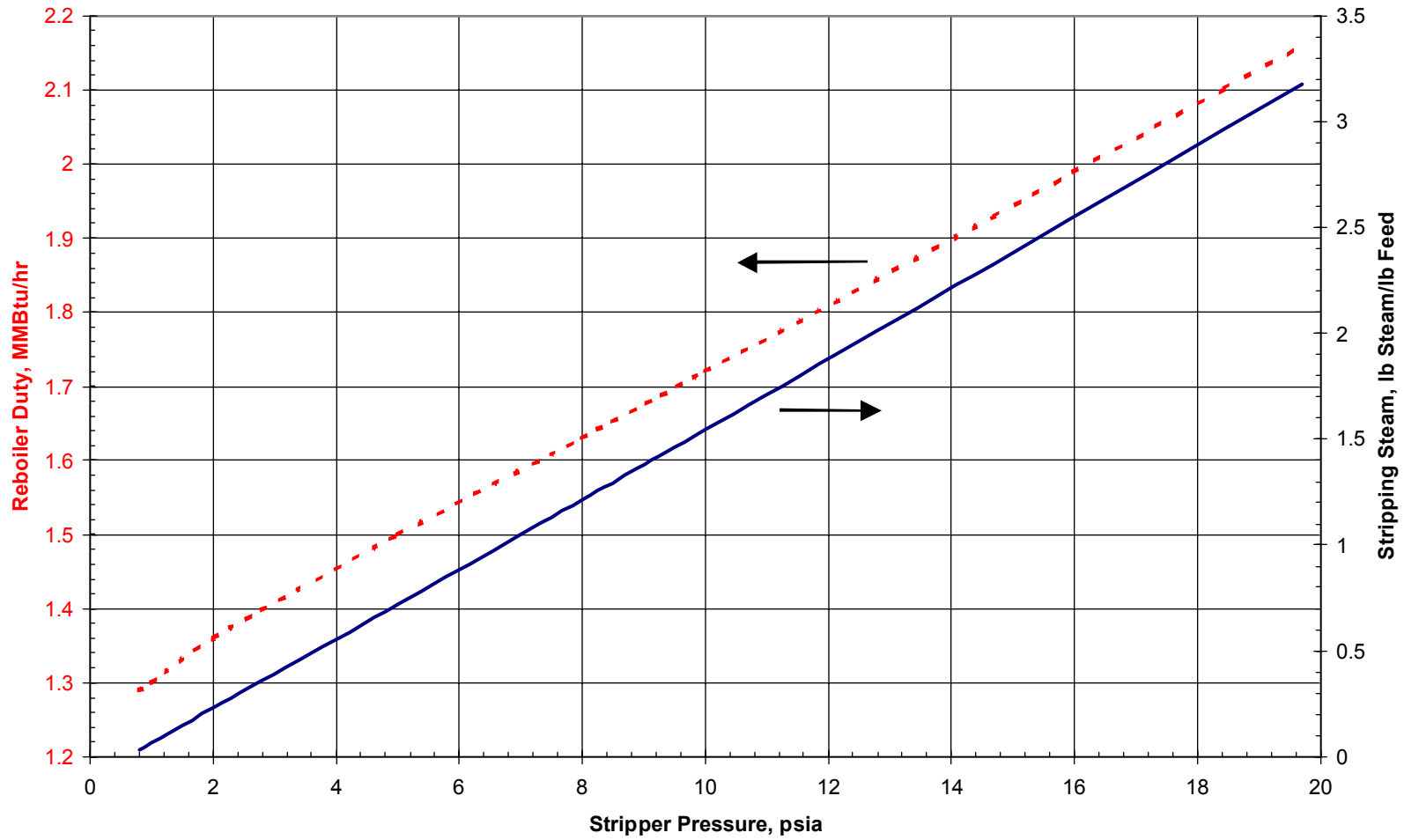
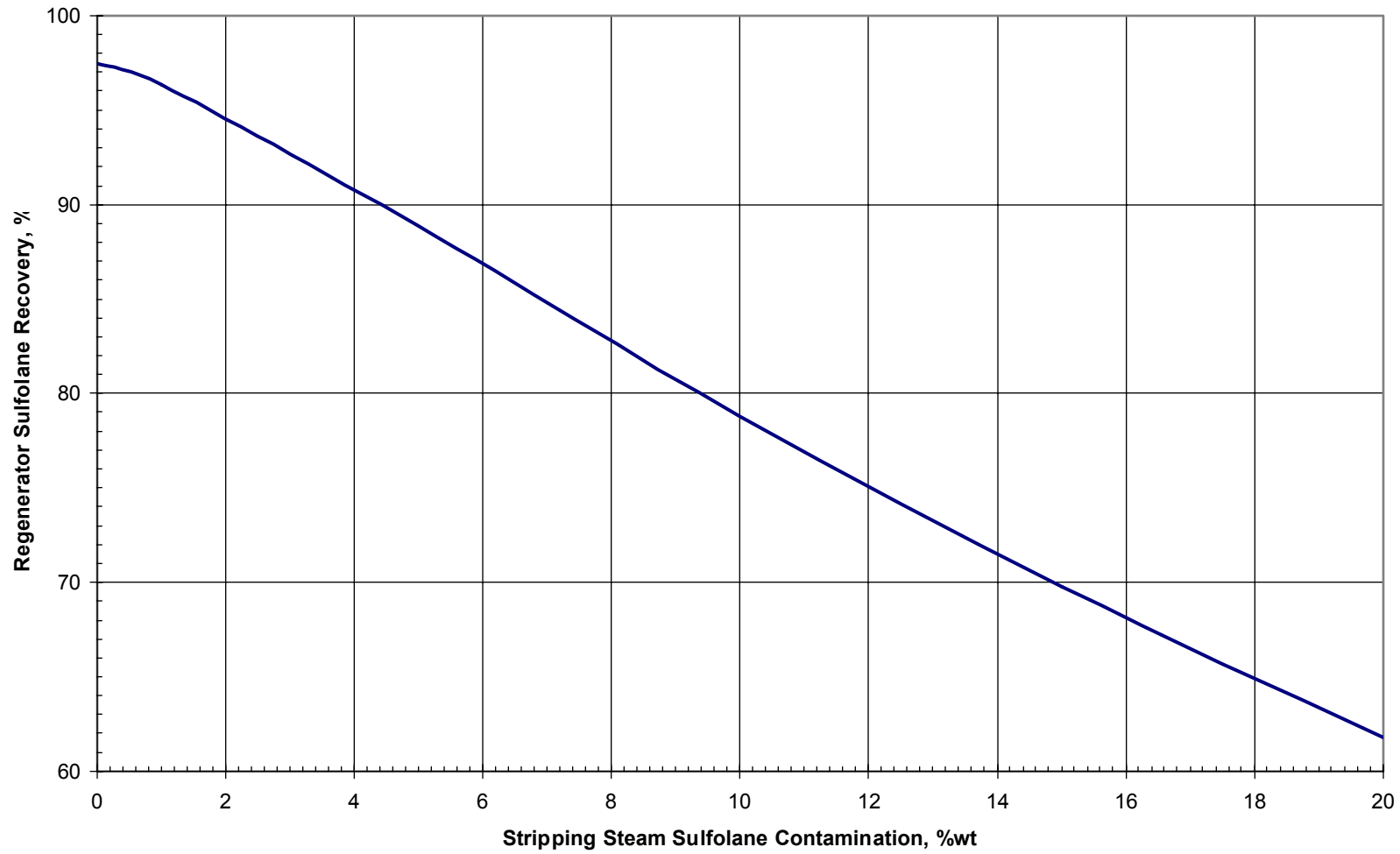


Figure 8 - Effect of Assist-Steam Sulfolane Content on Regenerator Sulfolane Recovery
NRTL Sim [10], 10 psia Regen Pressure, 360 °F Feed, 360 °F Bottoms Temperature, Constant 1.6 lb Steam per lb Regen Feed w/Increasing Contamination



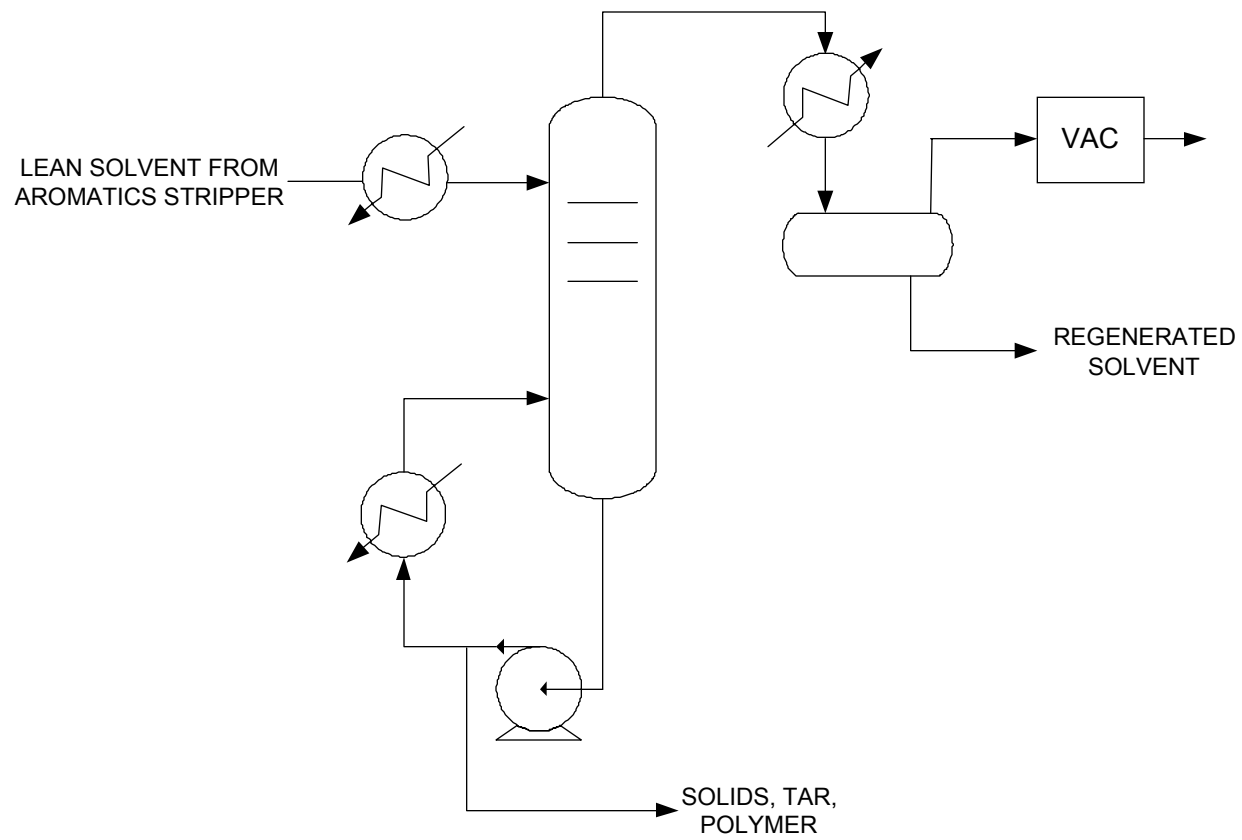
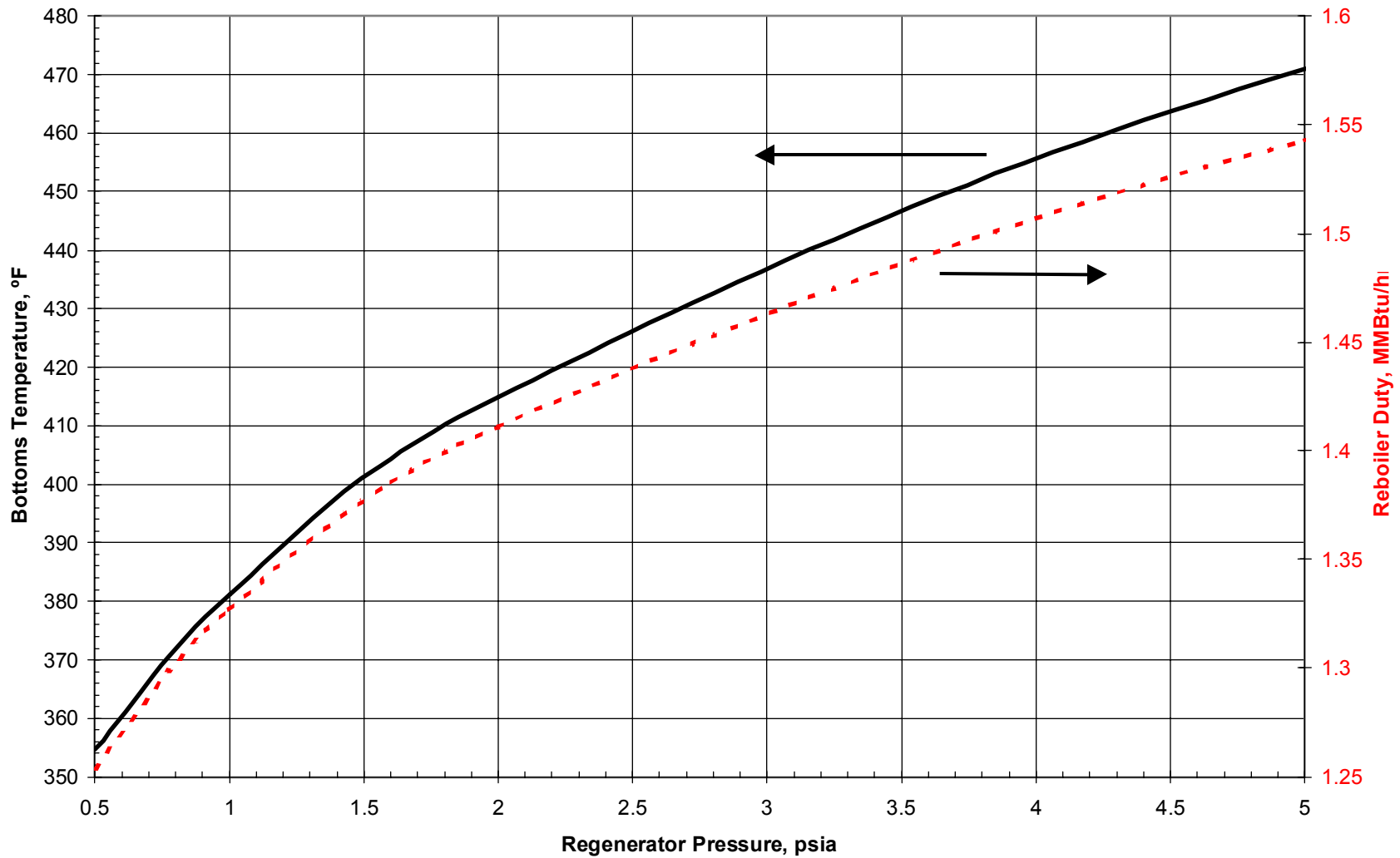


Figure 9 - Reboiled Regenerator

Figure 10 - Effect of Reboiled Regenerator Pressure on Reboiler Duty & Bottoms Temperature

NRTL Sim [10], 11 gpm Regen Feed, 360 °F Feed Temperature, 0.4 wt% Heavies in Feed, 97% of Sulfolane in Feed Recovered



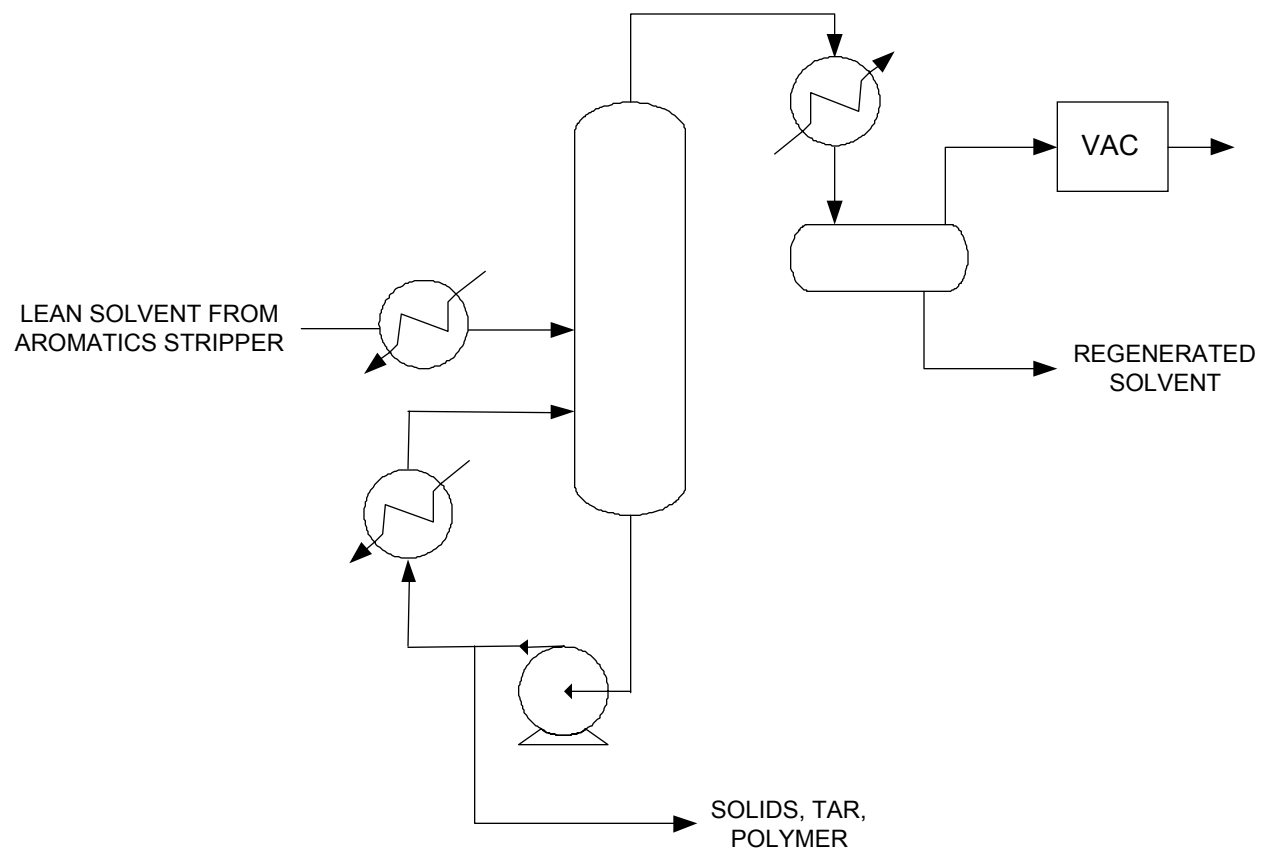


Figure 11 - Flash Regenerator

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Author's Previous Publications

- "Heat Integration Complicates Heat Pump Troubleshooting,"* D. Schneider, Hydrocarbon Processing, May, 2002.
- "Improve Catalyst Removal Methods,"* D. Schneider, Hydrocarbon Processing, October, 2000.
- "Practical Process Hydraulics Considerations,"* D. Schneider, M. C. Hoover, Hydrocarbon Processing, August, 1999.
- "Plant Power Failure and its Indirect Effects: a Case Study,"* D. Schneider, Petroleum Technology Quarterly, Winter 1998/99.
- "Select the Right Hydrocarbon Molecular Weight Correlation,"* D. Schneider, Chemical Engineering Progress, December, 1998.
- "Steady-State Simulators for Design,"* D. Schneider, Chemical Processing, December, 1998.
- "Build a Better Process Model,"* D. Schneider, Chemical Engineering Progress, April, 1998.
- "Deep Cut Vacuum Tower Processing Provides Major Incentives,"* D. Schneider, J. Musumeci, Hydrocarbon Processing, November, 1997.
- "Debottlenecking Options and Optimization,"* D. Schneider, Petroleum Technology Quarterly, Autumn 1997.
- "Programming, It's not Just for Programmers Anymore,"* D. Schneider, Chemical Engineering, May, 1997.
- "Deep Cut Vacuum Tower Incentives for Various Crudes,"* D. Schneider, J. Musumeci, L. Suarez, Presented @ the AIChE 1997 Spring Nat'l Mtg.
- "Process Simulation: Matching the Computer's Perception to Reality,"* D. Schneider, Presented @ the AIChE 1997 Spring Nat'l Mtg.
- "Debottlenecking Economics - Maximizing Profitability with Minimum Capital,"* D. Schneider, Presented @ the NPRA 1997 Annual Mtg.
- "Analysis of Alky Unit DIB Exposes Design, Operating Considerations,"* D. Schneider, J. Musumeci, R. Chavez, Oil & Gas Journal, September 30, 1996.
- "How to Calculate Purge Gas Volumes,"* D. Schneider, Hydrocarbon Processing, November, 1993.