

SRU simulation: getting the properties right

Reliable, predictive simulation software for SRUs requires recognition of many of the unique properties and behaviours of sulphur

ANAND GOVINDARAJAN, NATHAN A HATCHER, CLAYTON E JONES and G SIMON WEILAND
Optimized Gas Treating, Inc.

There are several commercially available tools for simulating the performance of sulphur recovery units (SRUs). The general basis for these simulators is often regression to a collection of plant performance data. However, the results are only as good as the data on which they are based.

Collecting accurate SRU performance data is fraught with difficulty, much of it associated with the collection and analysis of samples. For example, gas samples from the reaction furnace must be very rapidly quenched, otherwise hydrogen keeps reacting. Samples containing water must have the water quickly removed to prevent further reaction. Careful attention must be paid to the metallurgy of sample containers because they can have catalytic activity — early catalysts were iron based, and even stainless steel is reactive towards sulphur dioxide. Material balances around SRUs require special techniques to work around analytical data limitations. Even when the data are accurate, simulators that depend on this kind of regression have only limited reliability when extrapolated to conditions outside the range of the basic data.

We have recently completed development of a simulation module for SRUs that has a more fundamentals oriented basis, including reaction kinetics of COS and CS₂ formation and ammonia, BTEX, and hydrocarbon destruction in the furnace. The furnace model includes non-equilibrium conversion of hydrocarbons to COS, CO, and other species as well as burner mixing characteristics, which affect

ammonia destruction. The Sulphur Converter model predicts profiles of dew points and conversion through converter beds as well as COS and CS₂ destruction profiles. Sulphur condensers have rigorous sizing and rating integrated into their simulation. The solubility of H₂S, H₂S_x and SO₂ in all liquid sulphur streams is calculated, with particular application to sulphur pits where air or another carrier can be used to sparge and sweep these volatile species from liquid sulphur. The SRU model can be fully integrated with upstream acid gas removal and enrichment processes, and with downstream TGTU quench and tail gas amine treating. Through the use of detailed, highly non-ideal aqueous ionic chemistry, it includes the effects of SO₂, heat stable salts, and monomethyl-monoethanolamine (MMEA, a degradation product of MDEA) on the performance of these units.

Developing reliable, predictive, simulation software for SRUs necessarily requires recognition of many of the unique properties and behaviours of sulphur. To a large extent, the uniqueness of these properties stems from the fact that sulphur occurs predominantly in three forms: S₂, S₆, and S₈. In liquid form, as temperature increases, the S₈ allotrope will polymerise to higher molecular weight forms. Its distribution amongst these allotropes is temperature dependent, and transition between forms occurs spontaneously, accompanied by substantial enthalpies of reaction. This article addresses several properties of sulphur.

Molecular formula and molecular weight of sulphur vapour

The most fundamental property of any compound is its molecular weight. Sulphur exists in several forms under conditions prevalent in SRUs. In the temperature range of interest in SRUs, sulphur vapour exists predominantly in the allotropic forms S₂, S₆, and S₈ with temperature dependent distribution amongst these forms. Thus, its molecular weight is temperature dependent and can be expressed in terms of the average number of sulphur atoms per molecule of sulphur. The enthalpy changes associated with the conversion of one species form into another makes the Claus reaction endothermic in the reaction furnace where the S₂ form dominates, but exothermic in converter beds where the S₆ and S₈ forms dominate. Conversion between forms also makes the molar flow rate of sulphur bearing streams variable because sulphur is not simply 'elemental sulphur' — it is actually a mixture of the different forms with variable molecular weight. This effect, however, is normally a minor one because sulphur concentrations in gas streams usually are not high, with vapour composition dominated by water and nitrogen from the air used in the combustion of H₂S to SO₂ in the furnace.

Figure 1 shows a comparison between the temperature dependence of the average number of atoms of elemental sulphur per mole of molecular sulphur as reported in the *GPSA Data Book*,¹ the experimental data^{2,3} and the simulator model. The model is

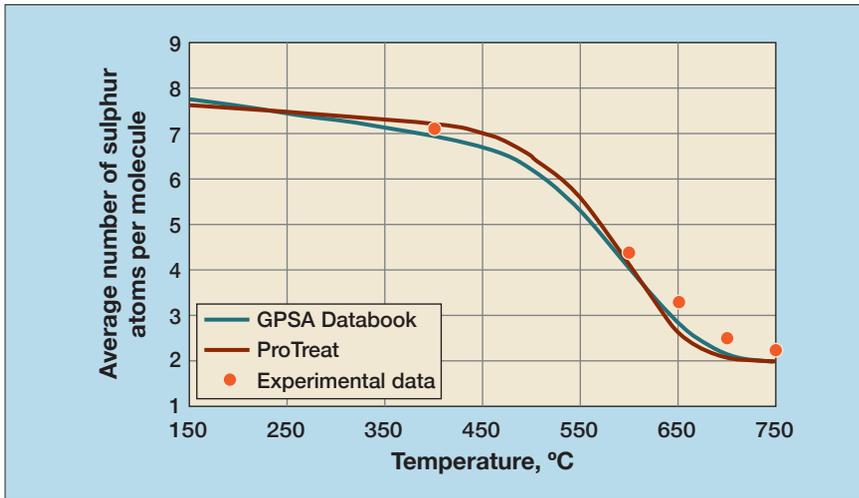


Figure 1 Temperature dependence of number of sulphur atoms in average molecule

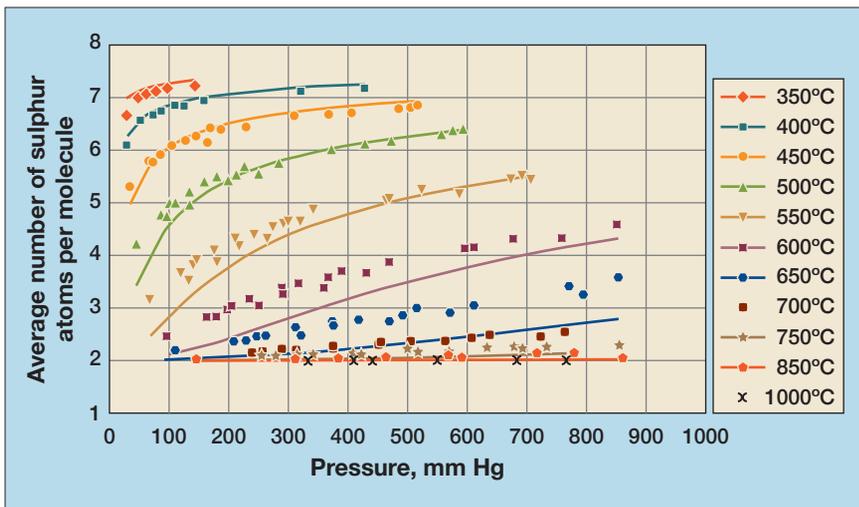


Figure 2 Experimentally measured sulphur molecular composition. ProTreat simulation predictions are solid lines

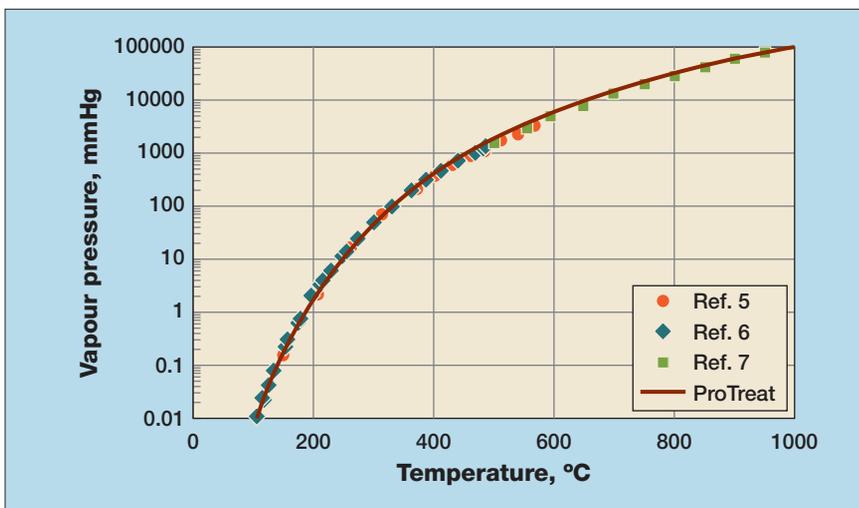


Figure 3 Experimentally measured vapour pressure of molten sulphur and the simulation model calculations

based on the reaction equilibria:



The reaction equilibrium constants

have the following form where, because pressures are low, vapour phase mole fractions rather than fugacities can be used with equal validity:

$$K_{p,1} = \frac{[y_{S_6}]^{1/3}}{[y_{S_2}]} P^{-2/3} * P^{-2/3}$$

$$K_{p,2} = \frac{[y_{S_8}]^{1/4}}{[y_{S_2}]} P^{-3/4} * P^{-3/4}$$

Here P is the total pressure and the y_i are mole fractions. The temperature dependence of the equilibrium constants obeys a van't Hoff type of equation with temperature dependent Gibbs free energies of formation regressed from tabular data⁴.

Without looking at the original references, it is not commonly known that **Figure 1** is at a pressure equal to the vapour pressure of sulphur at temperatures below its normal boiling point, and equal to one atmosphere at higher temperatures. The points in **Figure 1** have been interpolated from the experimental data of **Figure 2**. The data in **Figure 2** are from two sources^{2,3} and are the result of P-V-T measurements of a known mass of sulphur to determine the average molecular weight of the sample of gaseous sulphur. These measurements were not included in the original tabular data⁴ that form the basis for the ProTreat model. Thus, the lines in **Figure 2** are model predictions and have been made independently from the data plotted in the figure. The simulation model is in reasonably close agreement with the measured data.

Liquid sulphur

Liquid sulphur is normally dominated by S_6 and S_8 rings, but at higher temperatures (above $\sim 160^\circ\text{C}$, 320°F) the rings open and the short linear chains begin to polymerise. As will become apparent, the opening of these rings and the subsequent polymerisation of liquid sulphur has a significant effect on H_2S and H_2S_x solubility, viscosity, and heat capacity. Dissolved H_2S and H_2S_x also affect viscosity.

Vapour pressure of liquid sulphur

An important property, and one from which the latent heat of vaporisation can be derived, is vapour pressure. **Figure 3** shows vapour pressure data from several sources, together with calculations from the simulator.

Latent heat of vaporisation

Heat of vaporisation is an important property in sulphur condenser calculations. Data have been taken⁵ and regressed for use in the simulation model. The data (Figure 4) form an unusual curve, first decreasing and then increasing with temperature. This is the result of the changing distribution of the S_2 , S_6 , and S_8 allotropes of sulphur with temperature. In reality, what is measured and presented as latent heat of vaporisation also includes the heats of reaction associated with the chemical reactions that occur as the sulphur composition changes between its allotropic forms.

Viscosity of pure liquid sulphur

Pure liquid sulphur exists mostly in the forms of S_6 and S_8 rings, but around 160°C the ring structure opens and the sulphur polymerises. This is reflected graphically in Figure 5 where viscosity data⁵ are compared with simulation results. In the vicinity of the transition temperature, the viscosity undergoes a three to four orders of magnitude change, going from being relatively easy to pump to almost non-pumpable. The simulator accurately represents this behaviour.

The basis of the solubility model is polymer chemistry coupled with vapour-liquid equilibrium. The model accounts for the anomalous behaviour of H_2S in sulphur, which shows H_2S becoming more soluble in sulphur as the temperature increases. In the region around 160°C, the normal six- and eight-membered ring structures of sulphur open, becoming linear segments. These polymerise, with the polymer chains being terminated by H_2S molecules. The polymeric sulphur chains are apparently of maximum length at about 187°C (368°F) and they start to shorten with further rises in temperature. As they shorten, the viscosity falls and the chains become shorter but more numerous and, because they all use H_2S for termination, the apparent solubility of H_2S rises as temperature increases. The reason for increasing solubility is chemical bonding of

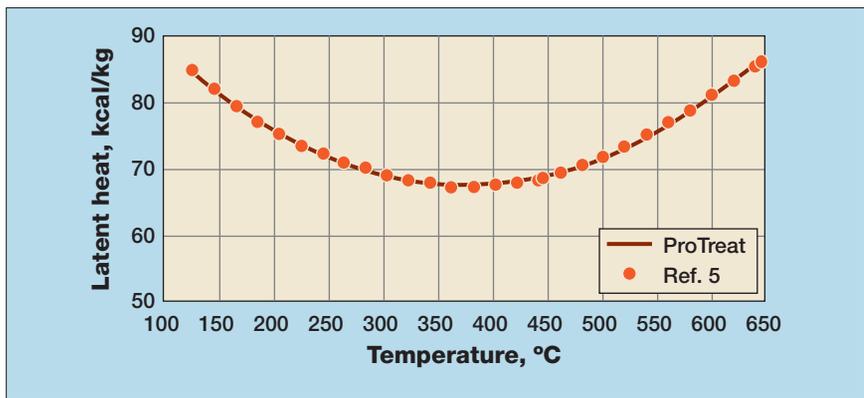


Figure 4 Latent heat of vaporisation of sulphur

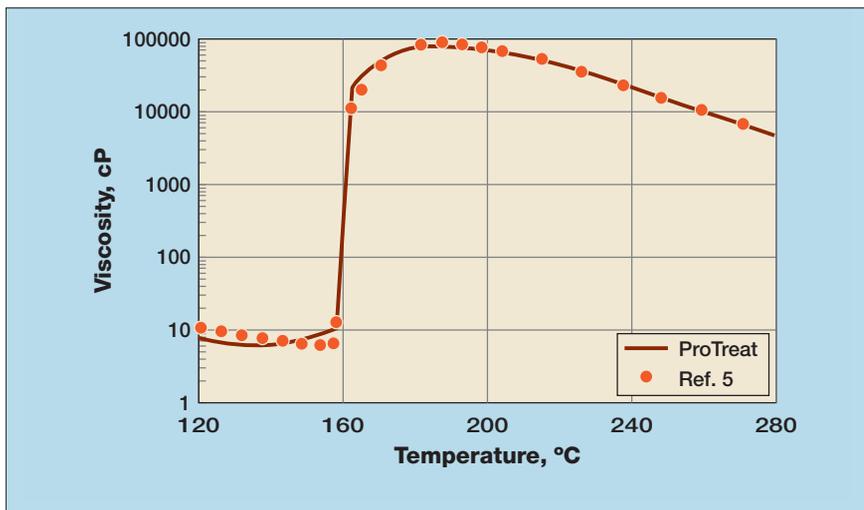


Figure 5 Viscosity of pure liquid sulphur

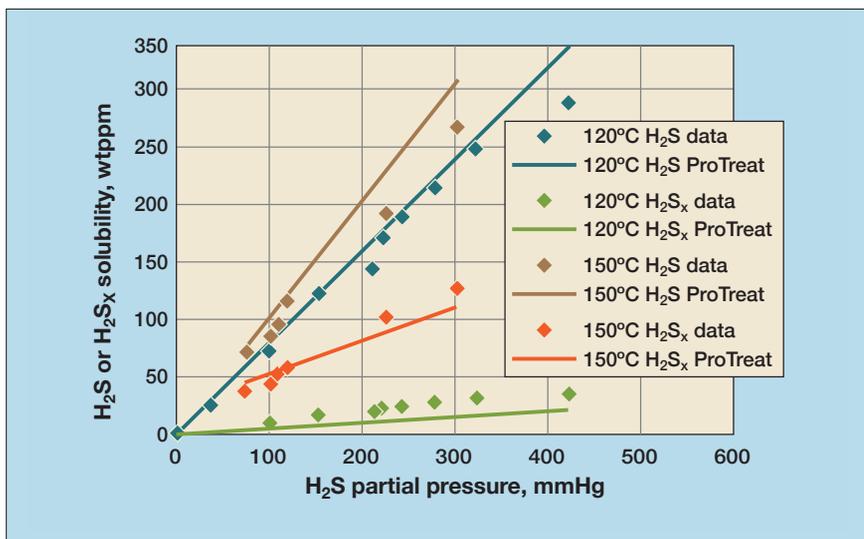


Figure 6 Solubility of H_2S and H_2S_x liquid sulphur.¹¹ Lines are model predictions

H_2S to sulphur. If solubility were purely physical, it would tend to fall with increasing temperature.

The model uses data from several sources.⁸⁻¹² A sample of the solubility data¹¹ is shown in Figure 6, while Figure 7 compares model predictions with viscosity data.^{3,5} In both plots, the lines have been calculated from

the same model. As expected, the higher the H_2S partial pressure, the higher the solubility. The linearity of Figure 6 might be interpreted as adherence to Henry's Law; however, Figure 6 says otherwise. The solubility is not that simple. Increased H_2S partial pressure results in reduced viscosity. One might argue that

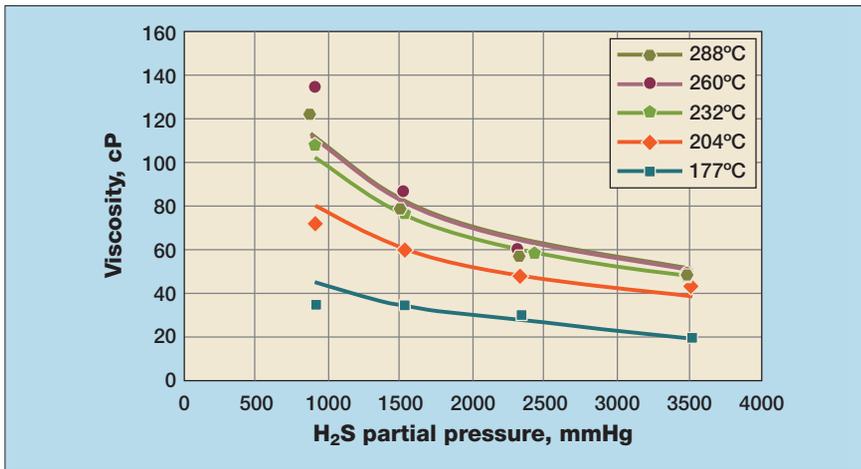


Figure 7 Effect of dissolved H₂S on the viscosity of liquid sulphur. Data^{3,5} vs model heat capacity

higher H₂S concentrations reduce the viscosity by diluting the polymer; however, a more likely explanation is shorter polymer chains that use more H₂S for chain termination. So the solubility is partially explained through a Henry's Law type of relationship, and partially through chemical reaction of H₂S as a sulphur chain terminator. Agreement between model and data is quite satisfactory.

Above 232°C (450°F) liquid sulphur is a sticky gum that cannot be processed, and below 120–121°C (248–250°F) it is a solid. Thus, it is only inside this range that the liquid heat capacity has any practical significance. Figure 8 shows heat capacity data¹, an artist-drawn line from the *GPSA Data Book*,¹ and the current simulation model.

The reason for the peak at 160°C is the same as for the sudden jump in viscosity at the same temperature, namely the opening of S₆ and

S₈ rings and polymerisation, with subsequent chain breakup and the attachment of H₂S at both ends as chain terminators. These are all reactions that act as additional sinks or sources for any heat added to the system, rather than having the added heat generate sensible heating alone.

Summary

Sulphur is one of nature's most unusual elements. It exhibits what at first glance seems like bizarre behaviour with sudden changes in viscosity and heat capacity, and counter-intuitive solubility of H₂S, all as functions of temperature and H₂S partial pressure. When understood in terms of transitions between multiple forms and sulphur's ability to polymerise, the behaviour of its properties can be understood.

It is important that any simulation tool at least reproduces the

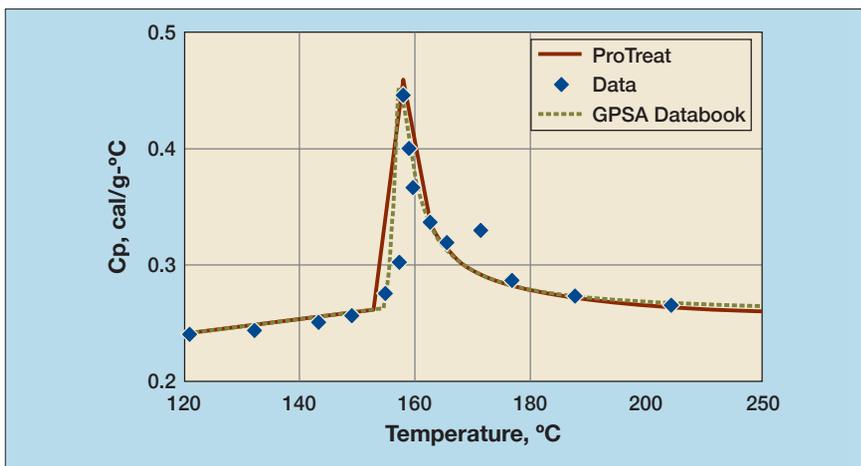


Figure 8 Heat capacity model (—) and data¹ for liquid sulphur

known properties of the components contained in the system. The ProTreat simulator calculates properties that correspond to measured data and uses chemistry in model development.

ProTreat is a mark of Optimized Gas Treating, Inc.

References

- 1 *GPSA Databook*, 12th Ed., Gas Processors Association, Tulsa, Oklahoma.
- 2 Braune H, Peter S, Neveling V, *Die Dissoziation des Schwefeldampfes*, Z. Naturforschung, 6a, 32-37, 1951.
- 3 Klemm W, Kilian H, Z. physik.Chem., 49B, 279, 1941, cited by [2].
- 4 *NIST JANAF Thermochemical Tables*, 4th Edition., Am. Inst. Phys., 1998.
- 5 *The Sulphur Data Book*, Tuller W N (ed.), Table 2-4, McGraw-Hill Book Co, New York, NY, 1964.
- 6 West, William A, Menzies A W C, The vapor pressures of sulphur between 100 and 550 with related thermal data, *J. Phys. Chem.*, 33(12) 1880-1892, 1929.
- 7 Rau H, Kuty T R N, Guedes De Carvalho J R F, High temperature saturated vapour pressure of sulphur and the estimation of its critical quantities, *J. Chem. Thermo.*, 5(2) 291-302, 1973.
- 8 Tobolsky A, Polymeric sulfur and other polysulfide polymers, *American Scientist*, 52, 359-364, 1964.
- 9 Wiewiorowski T K, Touro F J, The sulfur-hydrogen sulfide system, *J. Phys. Chem.*, 70, 234-238, 1966.
- 10 Touro F J, Wiewiorowski T K, Viscosity-chain length relationship in molten sulfur systems, *J. Phys. Chem.*, 1, 239-241, 1966.
- 11 Marriott R A, Fitzpatrick E, Lesage K L, The solubility of H₂S in liquid sulfur, *Fluid Phase Equilibria*, 26, 69-72, 2008.
- 12 Rubero P A, Effect of hydrogen sulfide on the viscosity of sulfur, *J. Chem. Eng. Data*, 9(4), 481-484, 1964.

Anand Govindarajan joined Optimized Gas Treating, Inc as Development Engineer in 2014. He holds a B.Tech degree from Anna University (India), MS and PhD from Oklahoma State University, all in chemical engineering.

Nathan (Nate) A Hatcher is Vice President, technology development for OGT. He holds a BS in chemical engineering from the University of Kansas. Email: Nathan.Hatcher@ogtrt.com

Clayton E Jones joined Optimized Gas Treating, Inc as a Software Development Engineer in 2012. He holds a BS in chemical engineering from McNeese State University and a MS in chemical engineering from the University of New Mexico.

G Simon Weiland recently joined Optimized Gas Treating as a Software Development Engineer. He holds a BS in chemical engineering from the University of Oklahoma.