UNIVERSITY OF CALGARY

Understanding why sulfur condensers work in Claus recovery

R. A. Marriott, C. B. Lavery and S. S. Nanji

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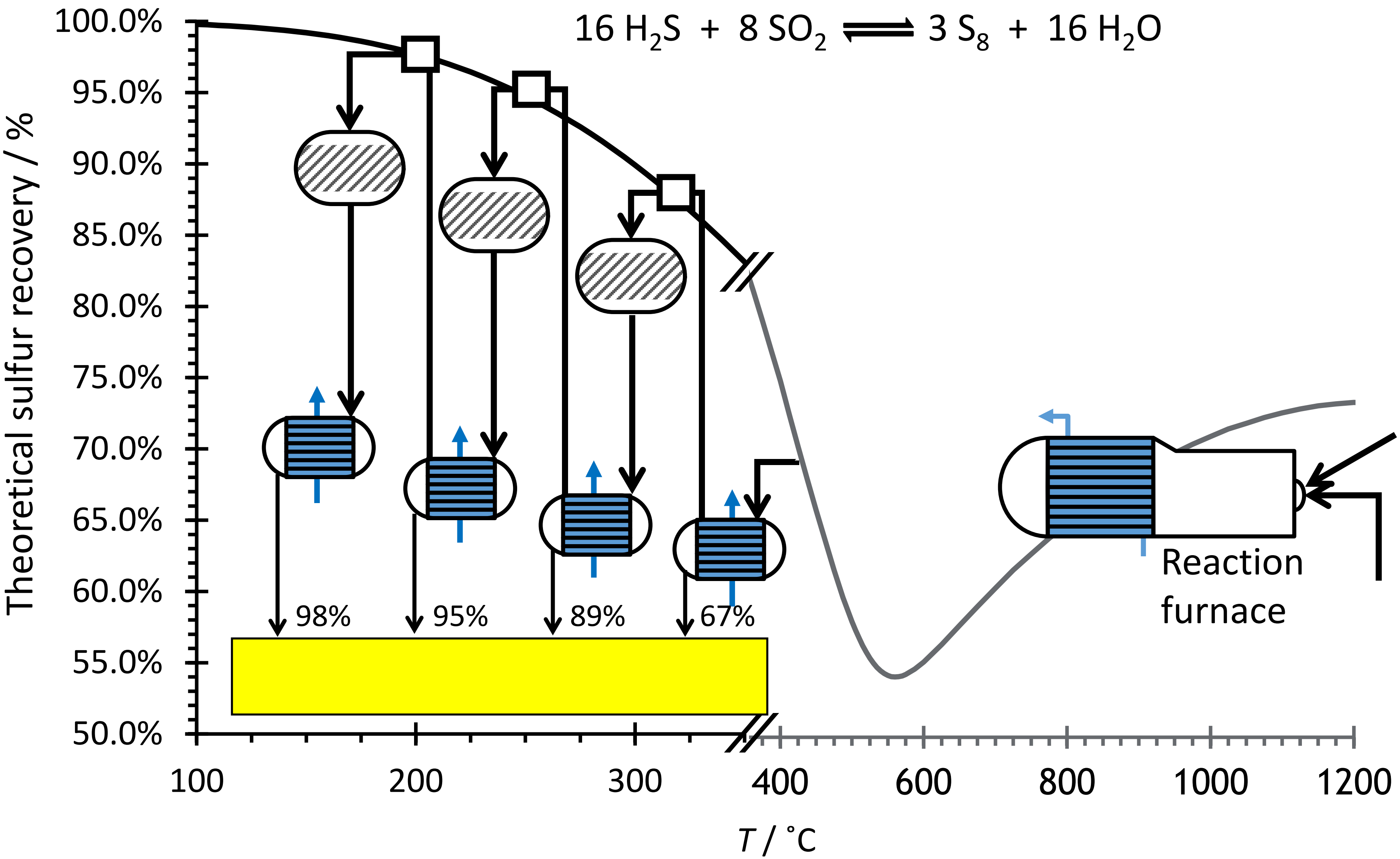
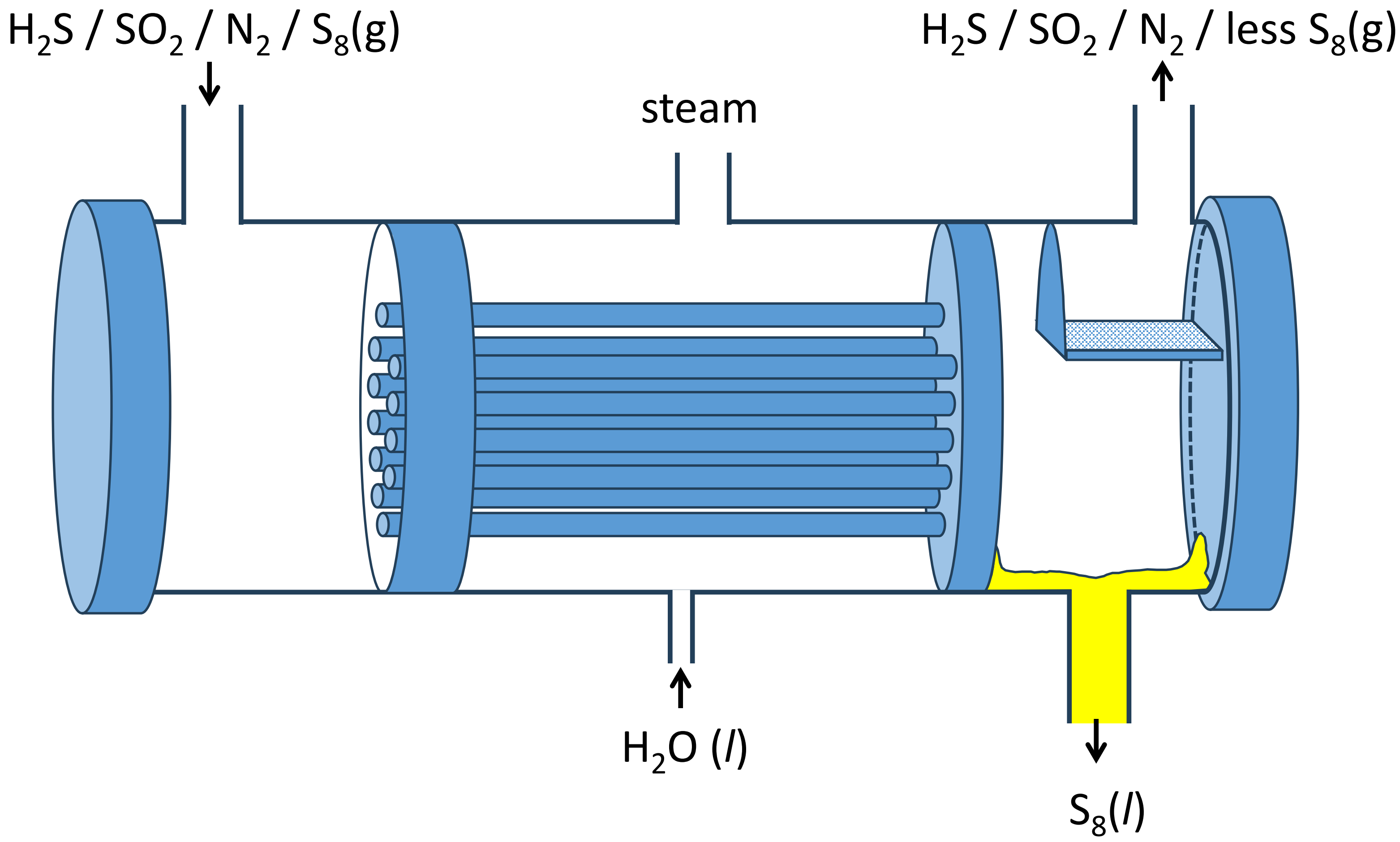
Sulfur condensers are required to control dew point and protect catalyst beds

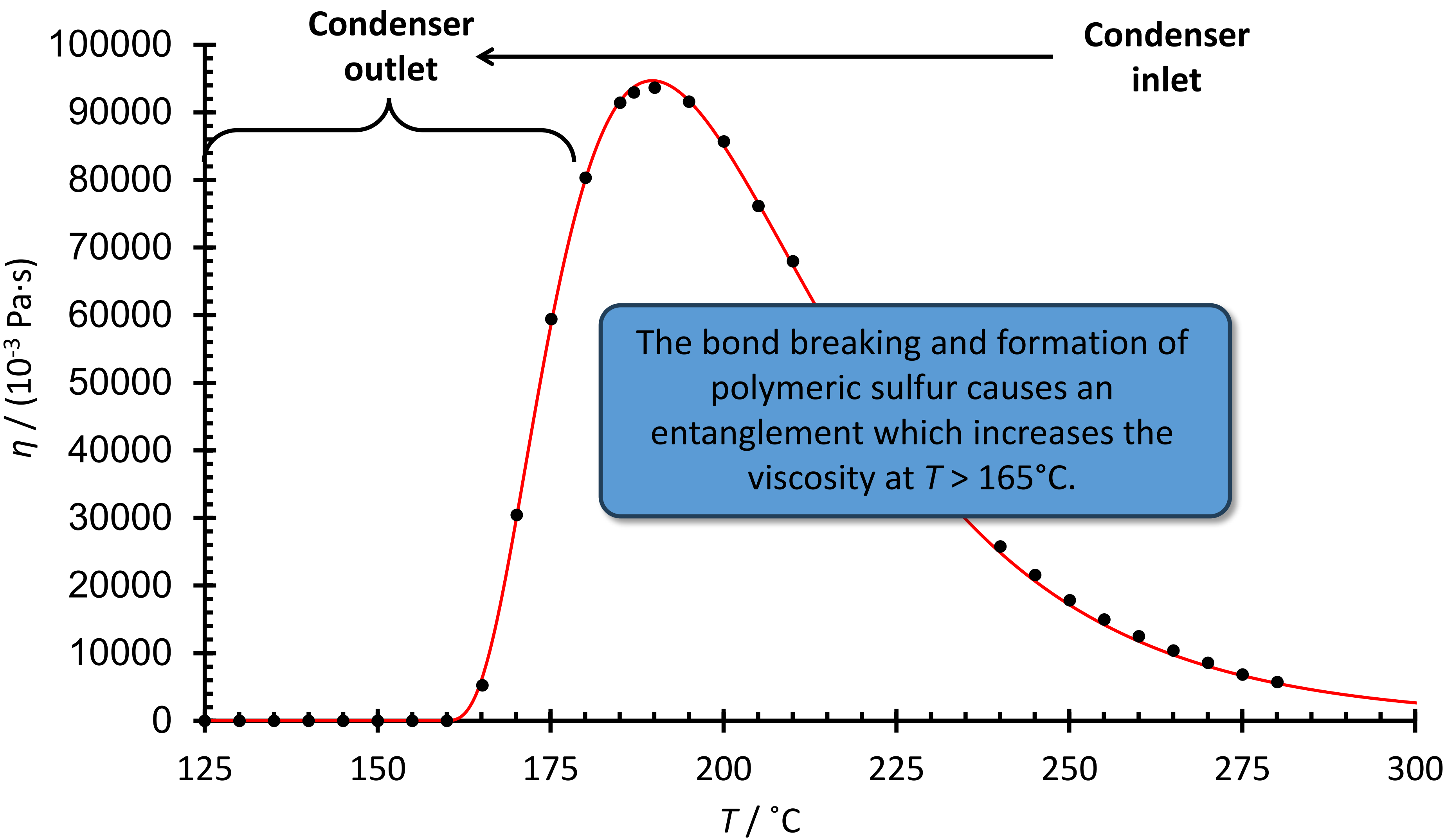
$$16\ H_2S + 8\ SO_2 \rightleftharpoons 3\ S_8 + 16\ H_2O$$



A chemist's simplified condenser diagram



But how did that liquid sulfur make it through the condenser?



The bond breaking and formation of polymeric sulfur causes an entanglement which increases the viscosity at $T > 165$°C.

M. J. Stashick, G. O. Sofekun and R. A. Marriott (2020) Modifying effects of hydrogen sulfide on the rheometric properties of liquid elemental sulfur. *AIChE J*, 66, e16225.

Explanations of sulfur flow through initial to final condensers

Known: Liquid sulfur goes through a maximum viscosity greater than 90,000 cP somewhere near 190 to 220°C. Pure sulfur will flow at $T < 160$°C.

Sulfur condensers work because:

(i) There is H_2S in the system which reduces the viscosity maximum for sulfur by limiting polymeric sulfur (by equilibrium)

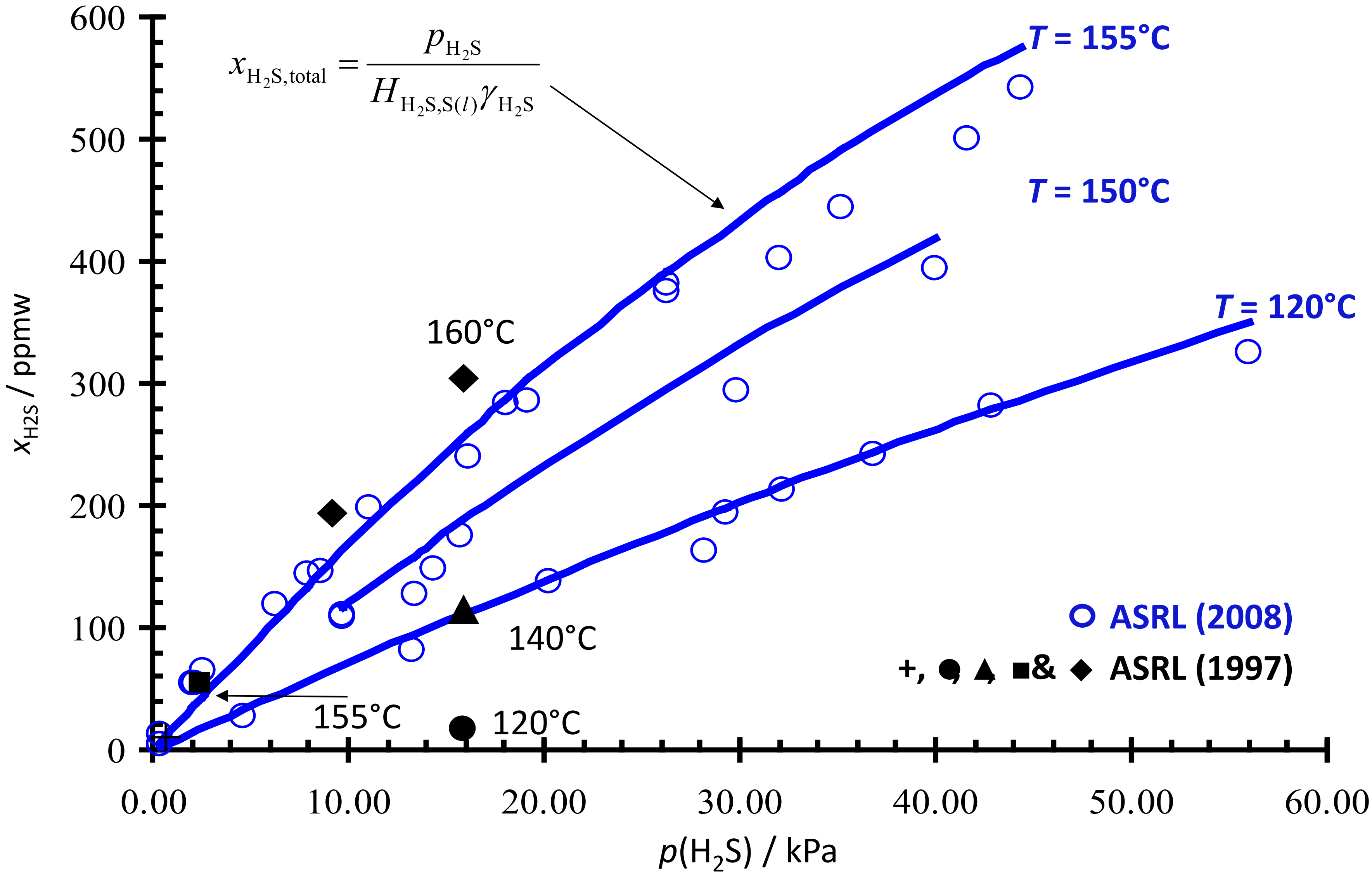
(ii) In the presence of H_2S, polymeric sulfur doesn't form during condensation

(iii) The sulfur condensation and residence in the tube is too fast for polymers to form regardless of the presence of H_2S

Are any or all of these things really true?

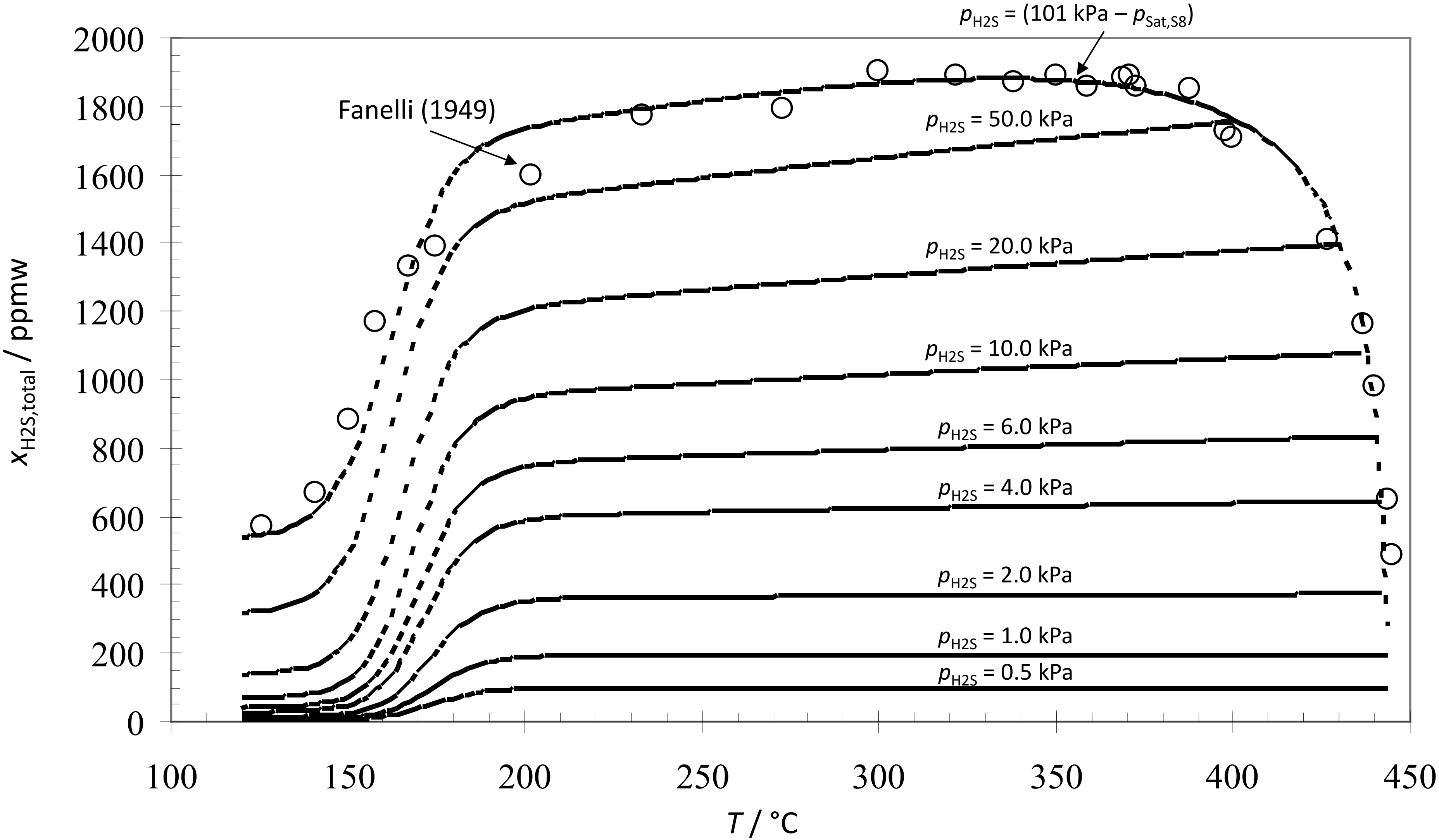
Do they need to be true?

So how much H_2S is in the condensed sulfur? A Henry's Law plot of H_2S in liquid sulfur



R. A. Marriott, E. Fitzpatrick and K. L. Lesage, Fluid Phase Equilibria 269, 69-72 (2008);
P. D. Clark, K. L. Lesage, E. Fitzpatrick and P. M. Davis, ASRL QB XXXIV(3), 1 (1997)

So how much H_2S is in the condensed sulfur? An updated model for low partial pressures of H_2S



R. Fanelli, Ind. Eng. Chem. 41, 2031 (1949).

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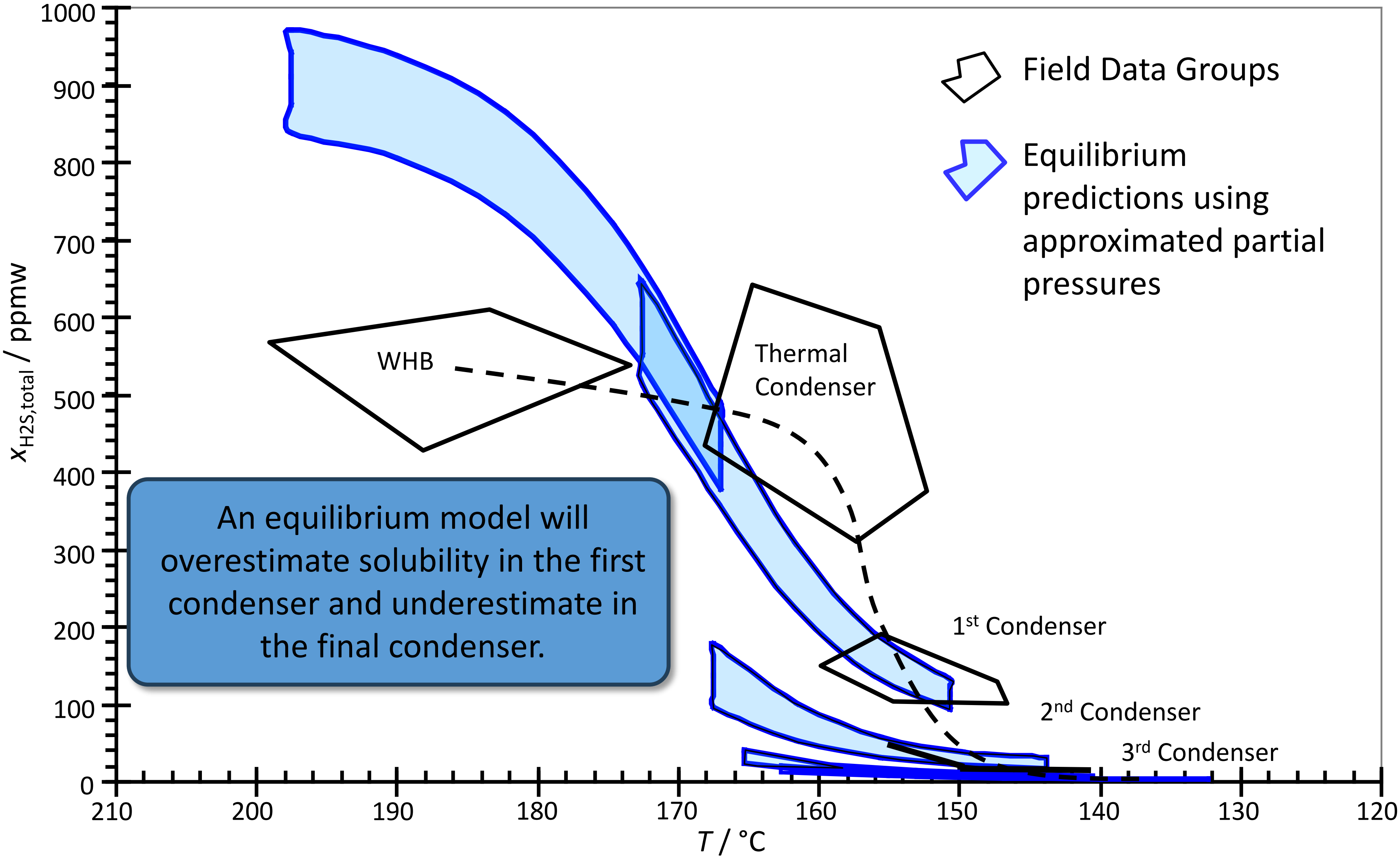
So how much H_2S is in the condensed sulfur?
H_2S equilibrium solubility compared to field data



An equilibrium model will overestimate solubility in the first condenser and underestimate in the final condenser.

Field data from P. D. Clark, K. L. Lesage, E. Fitzpatrick and P. M. Davis, ASRL QB XXXIV(3), 1 (1985)

So how much H_2S is in the condensed sulfur?
H_2S equilibrium solubility compared to field data

In 2008 we compared a new model to field data from Astrakhan and Orenburg gas plants (540, 154 & 21 ppm H_2S) in addition to the previous Western Canadian plants.

Learning: if we fix the quench temperature at T = 165°C, our model matches the field data.

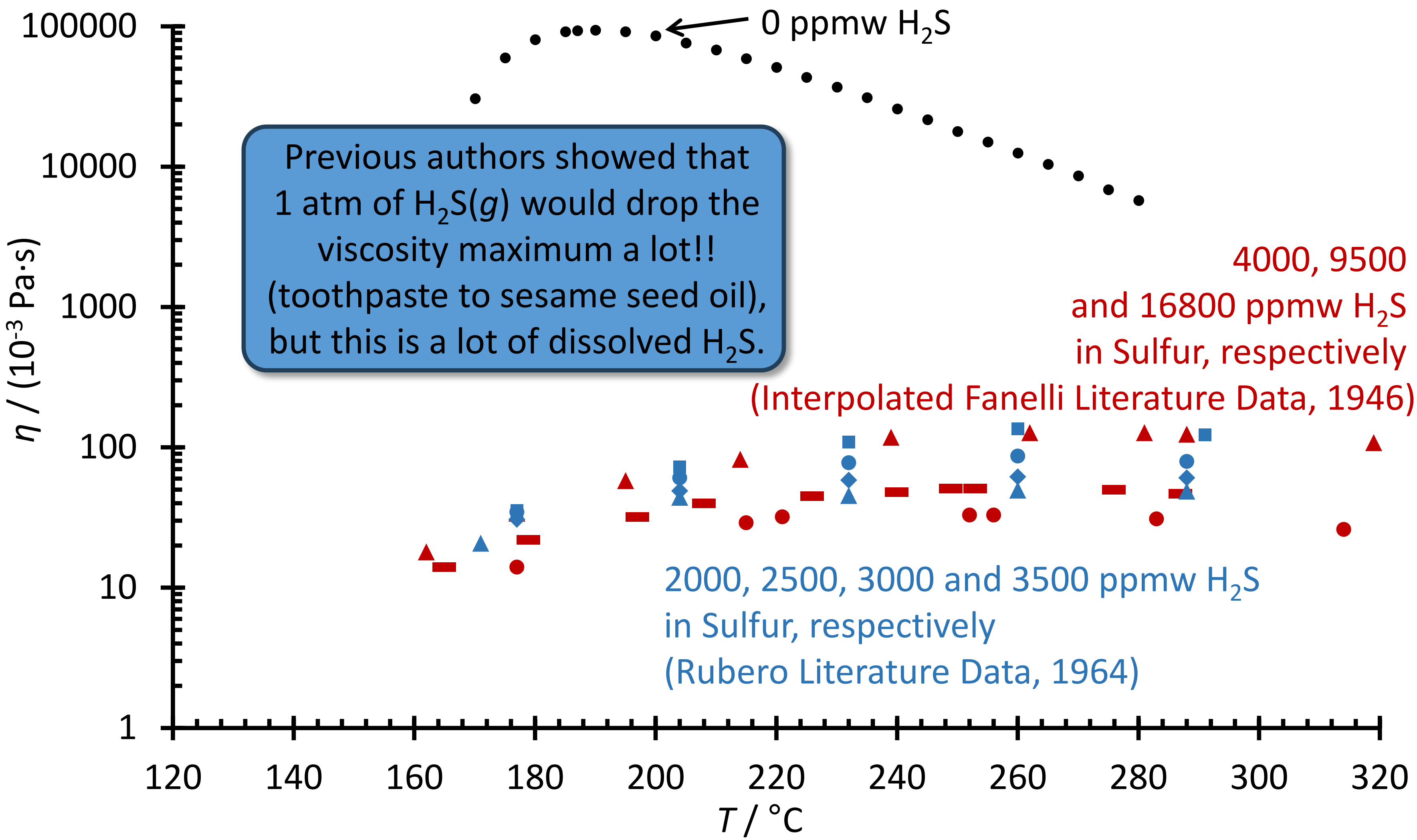
- H_2S_x formation is labile during condensation for $T > 165$°C
- The H_2S_x formation/degradation reaction is quenched at ~165°C

When we combine all condenser streams, they can be 300 ppm ($H_2S + H_2S_x$) for the pit liquid sulfur (depending only on H_2S partial pressure in the condensers; T_{eq} = 165°C)

Could 21 to 600 ppm total dissolved H_2S be enough to bring the viscosity maximum down low enough to flow?

R. A. Marriott, E. Fitzpatrick and K. L. Lesage, Fluid Phase Equilibria 269, 69-72 (2008)
P. D. Clark, K. L. Lesage, E. Fitzpatrick and P. M. Davis, ASRL QB XXXIV(3), 1 (1985)
Z.F. Ismagilova, R.R. Safin, F.R. Ismagilov, Chem. Technol. Fuels Oils 40 (2004) 279–283.

Sulfur viscosity with dissolved $H_2S + H_2S_x$



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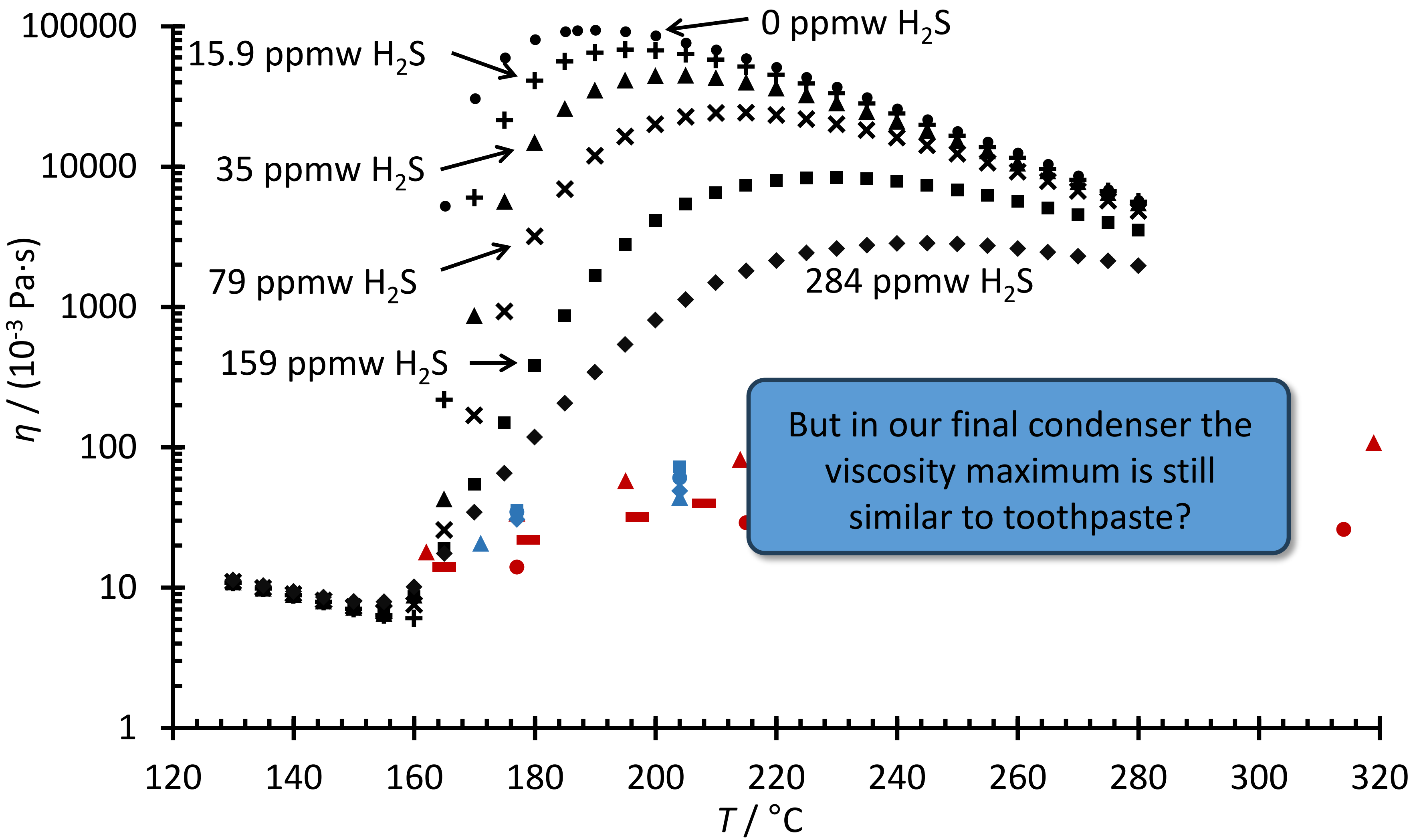

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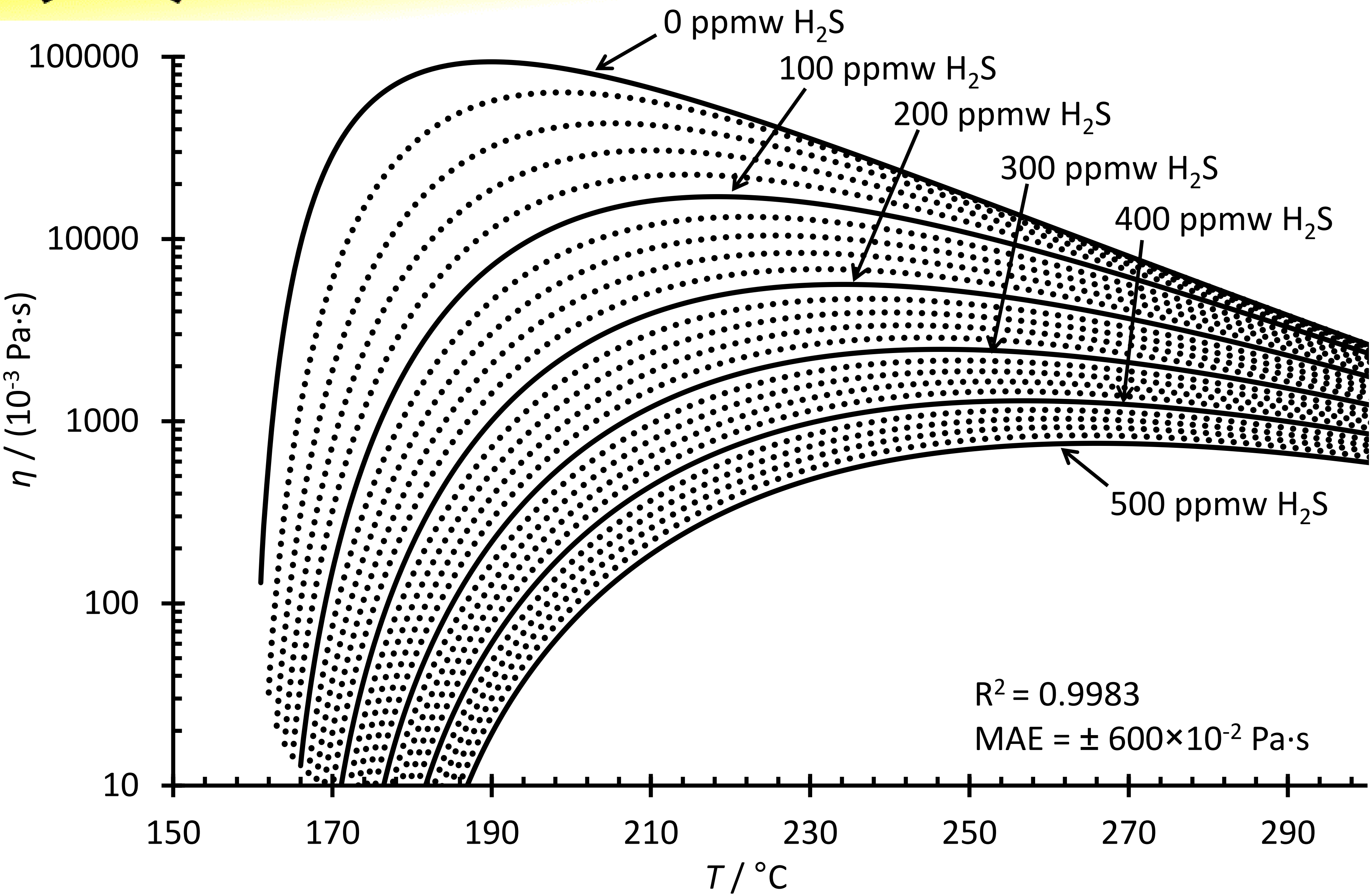

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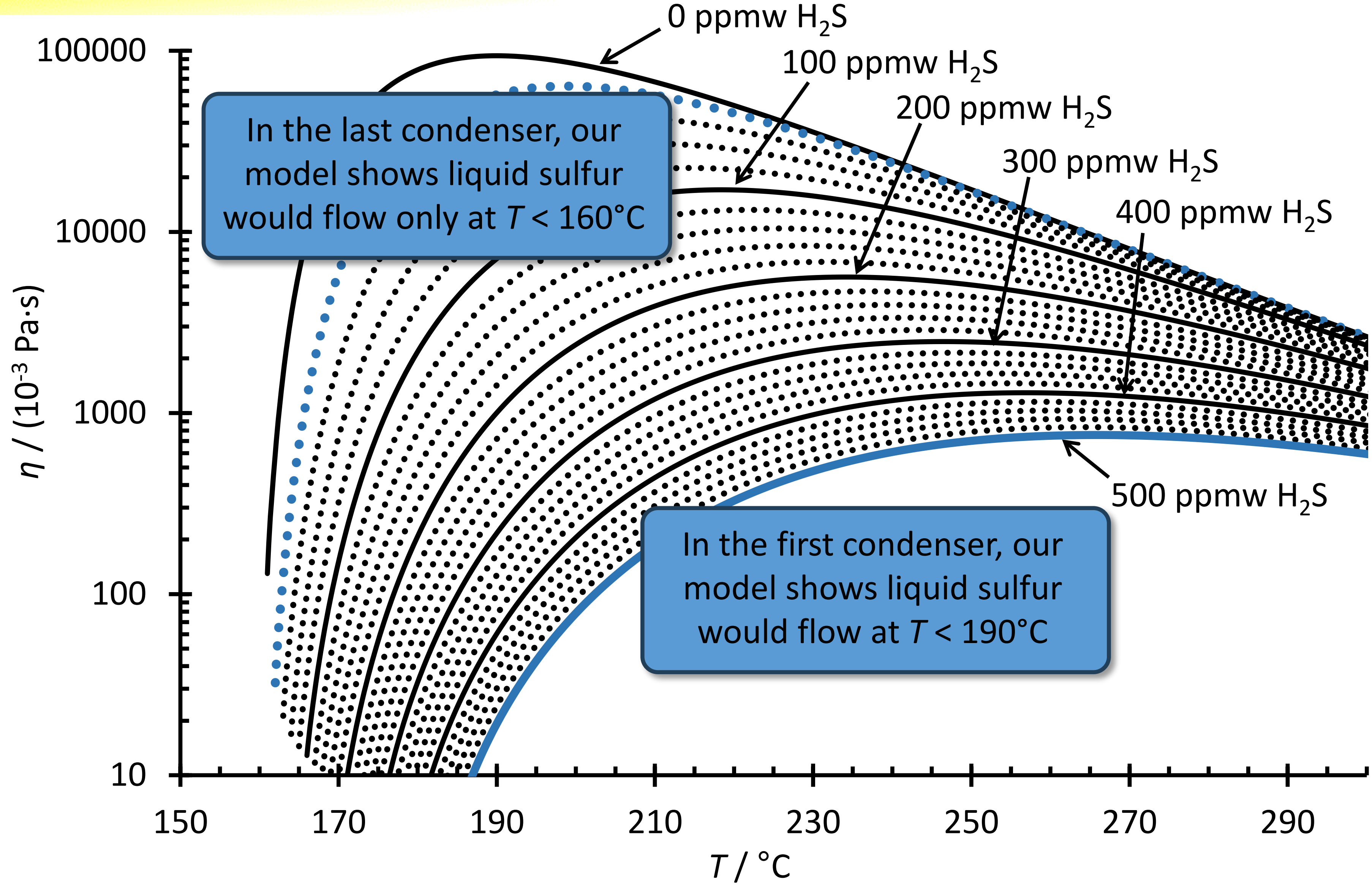

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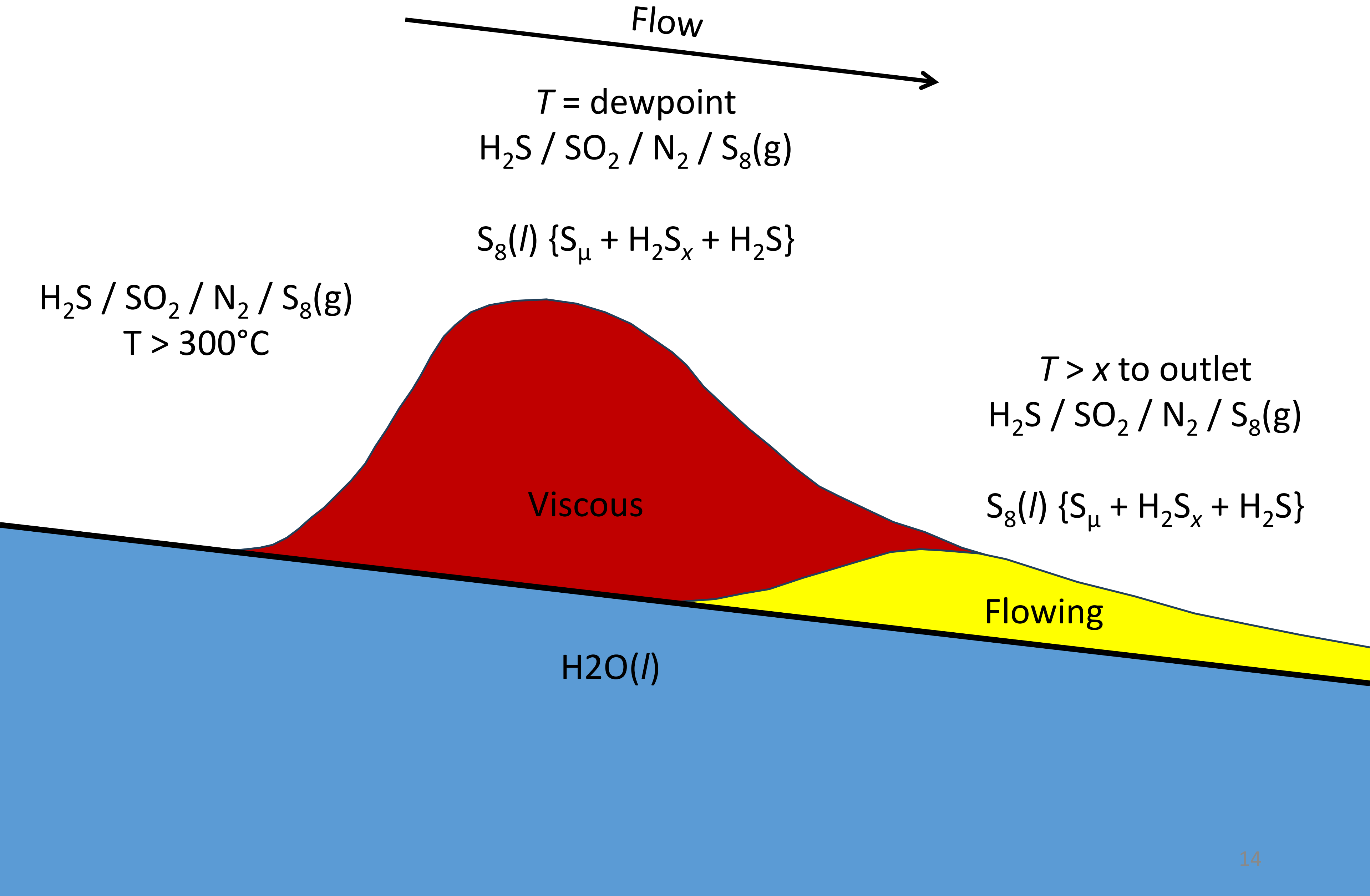
Returning to our condenser tube



Conclusions and future work

- Based on the past 40 years of research, it would appear that sulfur goes through a viscous phase within the condenser tubes
    - There is not enough H_2S in the first (or intermediate) condenser to lower the liquid sulfur viscosity maximum
    - There is enough H_2S in the first condenser to increase the lambda onset (flowing temperature) to $T > 160°C$; however, the polymeric sulfur is still there
- It's the steam pressure or exit temperature (skin temperature) which allows for sulfur flow
- Too much condensation could overcome the conversion rate to flowing liquid, which would overwhelm the tube(s) [ever happen?]
- How did Bacon and Fanelli purify their sulfur in 1942 if they didn't have high purity Claus sulfur?

R. F. Bacon, R. Fanelli, *Ind. Eng. Chem*. 34:1043–1048 (1942).

Thank you

- Abu Dhabi National Oil Company (ADNOC)
- Aecometric Corporation
- Ametek Process Instruments/Controls Southeast Inc.
- Axens
- Bechtel Energy Technologies & Solutions, Inc.
- Bryan Research & Engineering, LLC
- Canadian Natural Resources Ltd. (CNRL)
- CES Energy Solutions/PureChem Services
- Chevron
- Con-Sul, Inc.
- ConocoPhillips
- Delta Controls
- Euro Support BV
- Evonik
- ExxonMobil Technology and Engineering Company
- Flint Hills Resources
- Fluor
- HEC Technologies
- Hess Corporation
- Hexion Inc.
- HJ Baker Sulphur Canada ULC
- Honeywell UOP
- Houston Refining, LP (a LyondellBasell company)
- Industrial Ceramics Ltd.
- Lummus Technology
- Nasato Consulting Ltd.
- Nova Chemicals
- ONEOK, Inc.
- Optimized Gas Treating
- Ovintiv
- P. Scott Northrop, Ph.D.
- Paqell
- PetroChina Southwest Oil and Gas Field Company/RINGT
- Phillips 66 Company
- Saudi Aramco
- SECURE Specialty Chemicals Corp.
- Shandong Junfei
- Shell
- Sulfur Recovery Engineering
- Sulphur Experts Inc.
- Sultran
- TC Energy
- Technip Energies
- UniverSUL Consulting
- Worley Comprimo

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