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A NEW PROCESS FOR COMMERCIAL EXTRACTION OF SULFUR FROM SOUR GAS

By

Laurance S. Reid, Member AIME, and F. Mark Townsend
School of Chemical Engineering, University of Oklahoma, Norman

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Discussion of this paper at the meeting is invited. Written discussions for publication should be sent to the Society of Petroleum Engineers office.

INTRODUCTION

Despite an apparent abundance of elemental sulfur at this time, a recent survey and forecast of sulfur supply and demand by Stanford Research Institute, reported in Chemical and Engineering News¹, indicates that reserves of Frasch sulfur may reach a peak and decline in the face of a rising demand for brimstone during the next decade. There is little doubt that economic pressure will dictate that sulfur be recovered from sources now considered uneconomical.

For example, consider the sweetening of sour natural gas as practiced by the petroleum industry. At present and for many years past, producers and transporters of natural gas have removed hydrogen sulfide by a variety of processes, notably water-amine, glycol-amine, phenolate, hot carbonate, iron sponge, etc. But sulfur is recovered from these acid gas streams only when it can be produced at rates of 10 tons per day or more by various modifications of the Claus process. As a result, a large volume of sour gas is processed daily in hundreds of small sweetening plants. The off-gases, containing hydrogen sulfide, are vented and burned, representing a substantial loss of a valuable, exhaustible resource. Obviously, improvement is a matter of economics

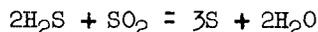
References and illustrations at end of paper

made possible by a higher price for sulfur, or recovery process improvement, or a combination of both.

The purpose of this paper is to present a new process development for sweetening sour gas and for effecting simultaneous recovery of elemental sulfur. Based on a reaction mechanism discovered by F. M. Townsend, the process has been developed by the authors to the pilot plant stage and it is known as the "Townsend Process". This process has several notable features: [a] Gas is sweetened and its sulfur compounds are converted to elemental sulfur in one step, [b] the sweet residue gas is effectively dehydrated, [c] the process is virtually insensitive to carbon dioxide, [d] it appears to be adaptable to a complete range of H₂S content regardless of whether gas sweetening or sulfur recovery is the prime objective, and [e] it can replace the Claus process in converting off-gases from sweetening processes of various types, and it promises to be especially effective where the CO₂ and/or heavier hydrocarbon content of such mixtures is excessively high.

Like the Claus process, this new process employs the reaction:

*U. S. and foreign patents pending. Licensed to The Hudson Engineering Corp., Houston, Tex.



in which the heat of reaction is -56.26 kilocalories and the free-energy change is -25.9 kilocalories at 25° C. However, the similarity ends there, for the reaction takes place in an organic solvent-water solution in the Townsend process. Although a large number of hygroscopic organic liquids may be employed with success, the preferred solvents are either diethylene glycol, or triethylene glycol in concentrations greater than 90 per cent glycol by weight. These solutions absorb sulfur dioxide readily, as shown in Fig. 1, act as catalyst, and help shift the reaction toward completion by binding the water formed. Hydrogen sulfide in the gas reacts with sulfur dioxide, whose concentration is carried in slight excess to react all H₂S; and elemental sulfur is formed in finely dispersed particles at the gas-liquid interface, resulting in a glycol-sulfur slurry.

TYPICAL APPLICATION

Numerous variations of the process are possible but Fig. 2 shows a typical application for treating sour natural gas where, in addition to recovering sulfur, sweet residue gas is desired. Referring to this diagram, sour natural gas enters the base of the reactor at atmospheric temperature and line pressure and ascends the reactor column where it is contacted by a descending stream of 98 per cent glycol, containing the required amount of SO₂, which is introduced into the top of the reactor. Upon contact, the reaction takes place forming sulfur and water. The sulfur is insoluble in glycol but the water is absorbed. Sufficient glycol is used so that its concentration is decreased to but approximately 95 per cent after absorbing all water produced in the reaction plus the water vapor content of the inlet gas.

Exit gas from the reactor rises into the high pressure absorber where it is contacted by a descending stream of concentrated SO₂-free glycol that enters at the top of the column. This stream absorbs the excess SO₂ and residual water vapor and drops into the reactor as shown. Sweet dry gas issues from the top of the absorber.

The counter-current flow arrangement of the reactor results in a temperature gradient in the reactor with temperature increasing toward the base of the vessel. The calculated temperature at the base of the reactor, processing various concentrations of hydrogen sulfide in a natural gas, is shown in Table 1. These temperatures are based on the assumption of natural gas in at 80° F, glycol in at 100° F, and gas out at 110° F.

Table 1

Variation of Temperature at Base of Reactor with Hydrogen Sulfide Concentration of Inlet Gas

H ₂ S, Vol. Per Cent	Temp., °F
1	120
10	200
20	215
40	225

The counter-current flow arrangement also permits taking advantage of higher reaction rates at the higher temperatures in the base of the reactor and the more favorable equilibrium conditions and greater per cent conversion at the lower temperatures which prevail in the top of the reactor.

Sulfur and glycol are separated, and any excess SO₂ stripped from solution, by heating the mixture to 250-275° F where the sulfur melts, stratifies and is withdrawn from the system. The separated glycol is reconcentrated, cooled and recirculated through the system where it [a] recovers any excess SO₂ from the residue gas leaving the process, [b] absorbs the necessary SO₂ required from the flue gases from a sulfur burner, and [c] is returned to the reactor. A portion of the sulfur produced is burned to supply the SO₂ required by the process.

A similar arrangement may be employed to process acid gas streams from conventional treating plans when [a] the CO₂ content of the mixture is too great to support combustion, or [b] where there is excessive hydrocarbon content. Otherwise, the acid gas stream may be split, as in the Claus process, a portion burned to form SO₂, and this flue gas re-mixed with the remaining sour gas which is cooled and discharged into the reactor.

THERMODYNAMIC CONSIDERATIONS

Since the reaction between hydrogen sulfide and sulfur dioxide is exothermic, higher equilibrium conversion should be obtained at lower temperatures. The theoretical considerations of Gamson and Elkins² show that equilibrium conversion of hydrogen sulfide to sulfur is approximately 95 per cent complete below 300° C and that it approaches 100 per cent conversion at atmospheric temperatures. However, a contact catalyst is required to carry out the reaction at all temperatures lower than 730° C. The aqueous glycol solution acts as the catalyst in the Townsend process.

The work of Gamson and Elkins indicates an increase in equilibrium conversion with increased pressure in the catalytic region below 730° C. This is due to the fact that, at high temperature, the sulfur formed by oxidation of hydrogen sulfide exists in the diatomic form. But, as the temperature is decreased, increasing amounts of

diatomic sulfur are converted to the octatomic form, and at 100° C, this conversion is virtually complete. Increased pressure enhances conversion in those cases where the number of molecules [not atoms] of reaction products are reduced in this manner.

At the lower temperature employed in the Townsend process, conversion is increased by maintaining the water formed in the reaction in the liquid phase. This is accomplished by solution in the concentrated glycol and favored by pressure in the reactor.

CORROSION

Since the Townsend process is virtually insensitive to carbon dioxide, evidence available to date indicates the probability that stress-relieved carbon steel components may receive effective protection from film-type corrosion inhibitors carried in the organic solvent. Where SO₂ is absorbed from sulfur burner gas, excess oxygen may require alloy construction or lining but this is a relatively small, low-pressure vessel and not excessively costly. Corrosion studies are under way at present to determine the extent of attack on mild steel, as well as the protection which may be afforded by various inhibitors, at various points in the process.

PROCESS ECONOMICS

The economic aspects of this process appear promising for several reasons. It involves one process instead of two, or possibly three contemporary processes employed in series to accomplish gas sweetening, residue gas dehydration and sulfur recovery. Gas shrinkage in the Townsend process is substantially less because it is virtually insensitive to carbon dioxide. Residue gas dehydration is inherent in the process and the sulfur recovery efficiency is at least equal to, or better than that obtained with the two-stage Claus process. The power requirement is smaller than that required by the aggregation of processes cited above, and the new process should be operated with the same labor required for a conventional amine-water sweetening plant. Substantial reduction in power requirements would result from development of large P-V pumps of the type produced by Kimray, Inc., bearing in mind that such a development would benefit other processes also.

Recovery of sulfur by means of the Townsend

process depends on the hydrogen sulfide content of the gas and upon the efficiency incorporated into the design of the process, since sulfur can be lost from but two points, [1] in the residue or effluent gas, and [2] from the sulfur burner gas absorber. If the gas contains only a few grains of H₂S per 100 cu ft, elemental sulfur must be supplied from an extraneous source to provide the sulfur dioxide requirement. However, as the concentration increases, process requirements for sulfur will be met, and surplus production will be available for marketing. It is anticipated that earlier industrial application of the process will be devoted to very sour gas where sulfur recovery is the prime objective. Sweetening of slightly sour gas may prove to be attractive for this reaction appears to be even more sensitive than the amine-water process in removing trace amounts of hydrogen sulfide.

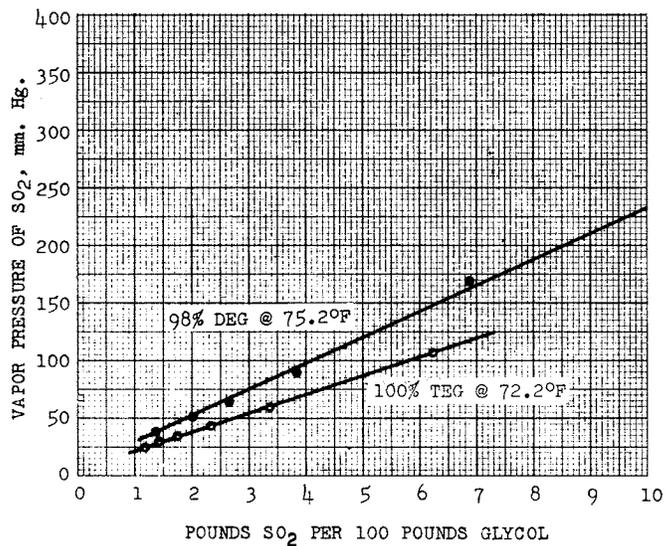
Comparative economic studies on relatively large plants indicate that the unit cost of treating gas by the Townsend process and the amine-water process are approximately the same when the CO₂ content of the gas is 1.0 per cent or more, without considering the value of the sulfur produced by the former. As the hydrogen sulfide content increases, the operating credit from sale of the sulfur reduces this charge. Based on present-day costs of equipment and labor and the price of sulfur, these studies indicate that sulfur revenue will offset operating charges when the hydrogen sulfide content ranges from 2 to 3 per cent.

CONCLUSION

This information is presented in response to growing interest in the Townsend process which, heretofore, has received scant publicity. The reaction mechanism is truly unique, the process is relatively simple, and it is adaptable to virtually every problem involving hydrogen sulfide removal and conversion. Full evaluation of its economic aspects in a semi-commercial installation is planned at an early date.

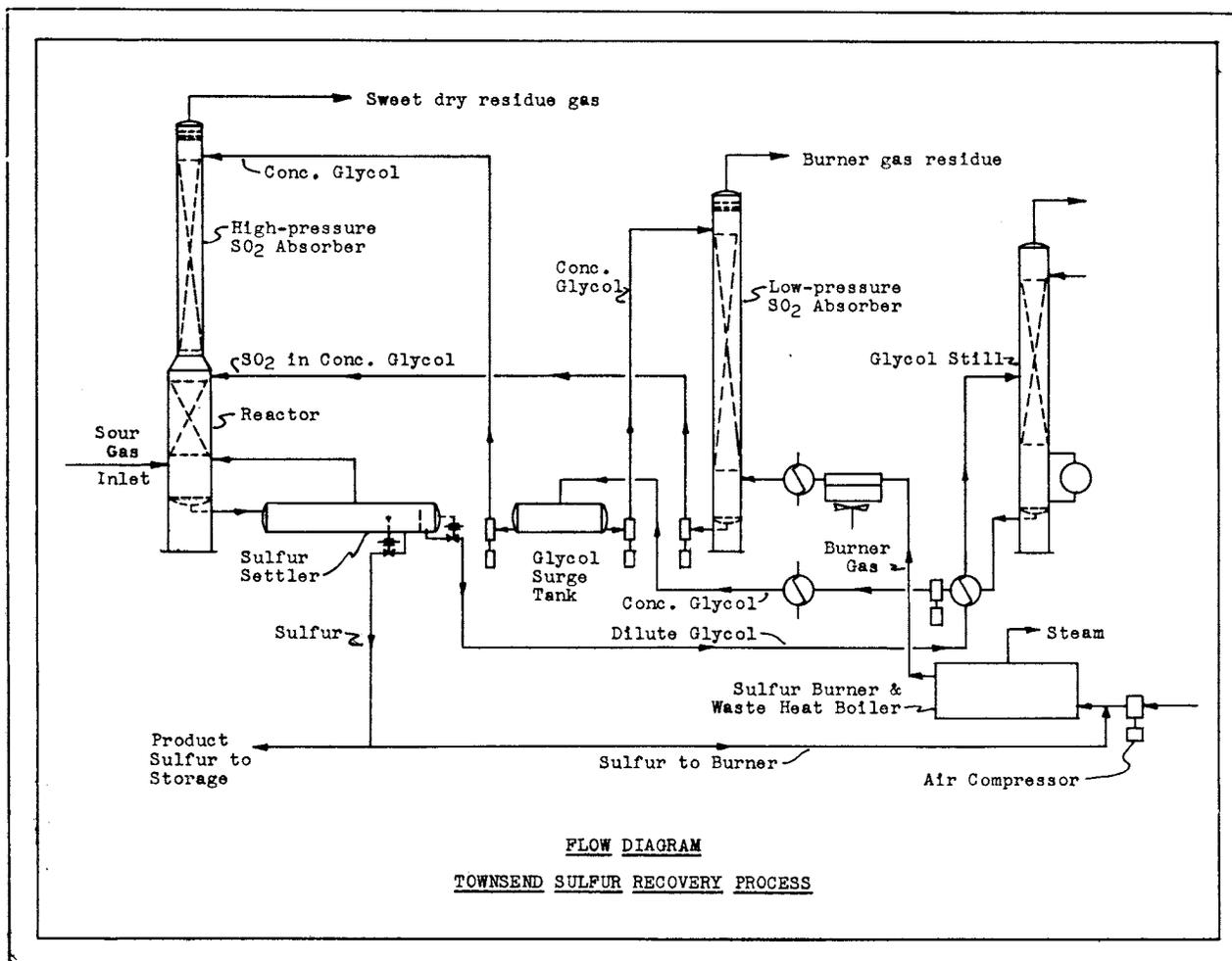
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SOLUBILITY OF SULFUR DIOXIDE IN
CONCENTRATED GLYCOL-WATER SOLUTIONS

Fig. 1



FLOW DIAGRAM
TOWNSEND SULFUR RECOVERY PROCESS

Fig. 2