

# SYNTHETIC FUEL GAS PURIFICATION

BY THE SELEXOL<sup>®</sup> PROCESS

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Processes for production of fuel gases from coal and petroleum come at a time when stringent requirements on sulfur emissions are being imposed. Indeed, part of the demand for these gaseous fuels stems from these requirements, because gases are relatively easy to desulfurize compared to liquids and solids.

The main contaminant to be dealt with is H<sub>2</sub>S. After removal H<sub>2</sub>S is converted to elemental sulfur, which is harmless and even sometimes profitable. Claus plants get first consideration for H<sub>2</sub>S conversion because they are well-known and economical. For high conversion and economy, Claus plants require a feed that is rather rich in H<sub>2</sub>S. A feed containing 20% H<sub>2</sub>S is considered a satisfactory Claus feed.

Concentrations as high as 20% are difficult to reach when treating synthetic fuel gases. In the production of high-Btu gas from coal, for example, the intermediate gas before methanation usually contains about 0.7 vol % H<sub>2</sub>S and 30% CO<sub>2</sub>. If both H<sub>2</sub>S and CO<sub>2</sub> are removed to low levels with a non-selective solvent, the

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Claus gas will be too lean for processing, about 2-3% in  $H_2S$ . The low-Btu gases would yield richer Claus feeds than this, but they too will yield gases too lean for economy and high conversion. A typical gas, for example, contains 0.7%  $H_2S$  and 8%  $CO_2$ , which would, with a non-selective solvent, yield a Claus gas containing only about 8-10%  $H_2S$ .

#### High Selectivity Required

Thus there is a need for highly selective solvents. Several selective solvents of both physical and chemical type are available but few have enough selectivity to remove  $H_2S$  to the very high degree required while holding  $CO_2$  absorption down to acceptable levels.  $H_2S$  content of product gases must usually be 4 ppmv or less. If the raw gas contains 0.7% or 7000 ppm, the degree of removal is then at least 99.94%, which may be higher after allowance for shrinkage due to  $CO_2$  absorption. If the Claus gas is to contain 20%  $H_2S$ , the amount of  $CO_2$  absorbed can only be four times that of the  $H_2S$ , or 2.8% of the original feed gas. Thus, if the original feed gas contained 30%  $CO_2$ , its degree of removal cannot exceed 9.35%; if 8%, 35.0%. The task is then to remove 99.94% of the  $H_2S$  while leaving 90.7% of the  $CO_2$  untouched in one example and 65% untouched

in the other.

Chemical solvents can remove acid gases with great efficiency and economy if the concentrations are low, but they cannot, as far as I know, achieve the kind of selectivity for  $H_2S$  required for Claus processing of synthetic fuel gases. The 4 commercially available physical solvents, including SELEXOL Solvent, can however achieve the required selectivity. The physical solvents, moreover, can remove certain other sulfur compounds which are non-acidic: COS, mercaptans, organic sulfides, and thiophenes. These must be converted to  $H_2S$  before they can be absorbed by chemical solvents. Some physical solvents, including SELEXOL, can simultaneously remove water to the standard specifications for pipeline gas, thus eliminating the need for auxiliary drying units.

#### Selective Absorption

Absorption systems forming ideal solutions show selectivities in proportion to pure-component vapor pressures, in accordance with Raoult's Law. For example, the vapor pressure of  $CO_2$  at  $60^\circ F$  is 752 psia; for  $H_2S$ , 230 psia. If the vapor and the liquid form ideal solutions, the relative solubility or selectivity will be  $752/230 =$

3.27; that is, under equivalent conditions,  $H_2S$  will have 3.27 times the solubility that  $CO_2$  will.

Good selective agents, however, will form non-ideal solutions in which both solutes are solvated,  $H_2S$  being more strongly affected than  $CO_2$ . The selectivity for these in SELEXOL Solvent at  $60^{\circ} F$  and 1000 psia is 9.16, about 2.8 times what it would be in an ideal solution. This nine-fold value for selectivity is not constant; it will vary somewhat with temperature, pressure, and composition of the system. Although there are large negative deviations from Raoult's Law, the solvation does not prevent easy desorption. Heats of desorption of  $H_2S$  and  $CO_2$  from SELEXOL Solvent are only about  $1/4$  of those found with chemical solvents.

Both the vapor phase, since it is under high pressure, and the liquid phase are very non-ideal. Thus many experimental VLE points are required for SELEXOL Solvent. These have been difficult to correlate over the wide ranges of composition, temperature, and pressure encountered in gas purification plants.

The selectivity inherent in the solvent, as expressed by a ratio of K-values, will not be realized unless the

solvent rate is kept low. If the solvent rate is near the minimum required for complete removal of  $H_2S$  or  $COS$  (i.e., if the Kremser absorption factor is somewhere between 1.0 and 1.5) it will be well below the minimum required for  $CO_2$  removal. In the examples used, only about 15 to 25% of the  $CO_2$  present may be removed, no matter how many contacts are provided in the absorber.  $CO_2$  will be quickly absorbed at the top of the absorber, reaching saturation in the first contact. As the solvent passes downward, absorbing  $H_2S$ , through the other contacts, no more  $CO_2$  will be absorbed. In this way a large fraction of the  $H_2S$  can be absorbed while holding the absorption of  $CO_2$  to a low level. Absorbers used for selective absorption will therefore have many contacts and low solvent circulation rates, in contrast to the bulk absorbers which will have relatively few contacts and high circulation rates.

The quantity of  $H_2S$  in gas from coal and crude oil is low, generally less than 1%. The  $CO_2$  concentration, on the other hand, can be high, as high as 30%. This means that the temperature profile down through the absorber will be dominated by  $CO_2$  rather than by the key component,  $H_2S$ .

The high partial pressure of  $\text{CO}_2$  will cause substantial absorption to take place at the top, causing a quick rise in temperature at the top contact, followed by a slower rise down through the other contacts as  $\text{H}_2\text{S}$  and smaller quantities of  $\text{CO}_2$  are absorbed.

The temperature profile in selective absorption will then normally be irregular, and the assumption of straight-line or equal-percentage variation down the tower cannot be made. At low solvent rates, moreover, the feed gas may further change the profile if the feed temperature is markedly different from absorber temperature.

K-values are sensitive to temperature; for example, the K-values for  $\text{H}_2\text{S}$  in SELEXOL Solvent in methane systems at 1000 psia increase about 15% for each  $10^\circ\text{F}$  rise in temperature. Thus, solubility will more than double between a drop from  $100^\circ\text{F}$  to  $40^\circ\text{F}$ . The temperature profile to be expected must therefore be taken into account in making a satisfactory design, and K-values must be available to permit designing as closely as possible to the temperatures which will prevail down through the tower.

The complete cycle of course, includes flashing, stripping, and heat exchange, which are carried out at a completely different set of pressures, temperatures, and compositions from that for absorption. The K-data required to calculate the results of these operations need to be predicted accurately over a wide range of conditions, which puts a strain on experimental VLE determinations and methods of correlation. Development of reliable K-data is probably the most important single factor in the success of a physical solvent, and offers the most difficult challenge in putting such processes into practice.

#### High-Btu Synthetic Gas

The SELEXOL process will be used in one of the new coal-gasification processes, the Bi-Gas process originated by the Bituminous Coal Research Corporation and sponsored by OCR and AGA. A demonstration plant is now planned for construction at Homer City, Pa.

To optimize methanation, some coal gasification processes require gas purification at three stages: removal of  $H_2S$  from gasifier effluent after CO-shift conversion and two stages of  $CO_2$  removal, one before and

one after methanation. The most important step is  $H_2S$  removal. The final product must be  $H_2S$ -free, the methanation catalyst must be protected from poisoning, and the  $CO_2$  off-gas must have so little  $H_2S$  in it that it can be safely released to the atmosphere. Further, the  $H_2S$  removed must be concentrated enough for economical conversion in a Claus plant.

A typical flowscheme for gas purification is shown in Fig. 1. The composition of the feed to the  $H_2S$  absorber is:

$H_2$	-	46.	vol %
$CO$	-	15.	"
$C_1$	-	8.	"
$CO_2$	-	30.	"
$H_2S$	-	0.7	"

The ratio of  $CO_2$  to  $H_2S$  is thus 43/1.  $H_2S$  must be removed to a high degree, at least to 4 ppmv (99.94% of that present in feed) to insure that the  $CO_2$  off-gas will contain less than 20 ppmv. This must be done in the presence of a large excess of  $CO_2$ , whose absorption must be suppressed in order to produce a sufficiently rich Claus gas,



something over 20% in H<sub>2</sub>S.

This is done by first removing H<sub>2</sub>S, using selective absorption and recycling some of the flashed gases. Stripping is with steam, which can be condensed out of the Claus plant feed, giving a mixture of CO<sub>2</sub> and H<sub>2</sub>S only. The Claus feed will contain more than 30% H<sub>2</sub>S, a concentration well over that required for economical Claus processing.

In the flowscheme shown, only 4 - 4½% of the CO<sub>2</sub> present in feed will be absorbed in the H<sub>2</sub>S removal system. This fraction can be varied by altering the number of stages in the absorber, the recycle rate, or the absorption temperature. Thus the costs of H<sub>2</sub>S removal can be balanced against the costs of conversion in the Claus plant to bring down the overall costs to a minimum.

Gas leaving the H<sub>2</sub>S removal section has essentially the same composition as that entering it, except that H<sub>2</sub>S is at 4 ppmv. This gas passes to the CO<sub>2</sub> removal section, where the H<sub>2</sub>S concentration will be further reduced to a few tenths of a ppm before methanation.

CO<sub>2</sub> can be removed both before and after methanation to suit any specification of methanator feed. Drying

of the final product to pipeline specification can also be arranged in a SELEXOL Process system, water leaving the system in stripping gas, which can be dry nitrogen coming from the air separation plant required to supply oxygen for gasification.

The CO<sub>2</sub> removal section is very simple. Besides the essential items of absorber, stripper, and pump, it has a flash tank and recycle compressor to keep methane losses very low, and a chiller to counter heat inputs from pumping and warm feed gases. CO<sub>2</sub> removal with SELEXOL Solvent is economical because most of the CO<sub>2</sub> is removed by simple flashing. Indeed, if CO<sub>2</sub> in the product could be 3.0%, regeneration could be by flashing alone. A lower CO<sub>2</sub> specification and a need for drying requires, however, that gas stripping be used.

#### Low-Btu Synthetic Gas

Another application which the SELEXOL Process seems to fit well is the purification of low-Btu fuel gases from coal. These gases, produced at intermediate pressures, are intended for turbine or boiler fuel. A typical gas from an air blown gasifier would have the following composition:

H <sub>2</sub>	-	15. vol %
N <sub>2</sub>	-	49. "
CO	-	22. "
C <sub>1</sub>	-	4. "
CO <sub>2</sub>	-	9. "
COS	-	.07 "
H <sub>2</sub> S	-	.7 "

After sulfur removal, this gas is the fuel for gas turbines or boilers. It is important to note that in this example we have shown that COS is contained in the gas. All of the products from coal gasification we have seen have included COS as well as H<sub>2</sub>S, in about a 1 to 10 proportion. Complete gas analyses have also shown lesser quantities of CS<sub>2</sub>, mercaptans, thiophenes, HCN, aromatics, and olefins. These can all be removed by SELEXOL Solvent without decomposition of the solvent. the solubility of COS, however, lies between that of H<sub>2</sub>S and CO<sub>2</sub>, so that it is more difficult to produce a concentrate of COS than it is to produce a concentrate of H<sub>2</sub>S. It can be successfully done, however, as this low-Btu gas example will show.

We have chosen severe requirements for treating this

gas. Total sulfur, including both  $H_2S$  and  $COS$ , is to be as close to 1 ppm as possible, while maintaining a Claus gas feed at 15% in total sulfur. The ratio between  $CO_2$  and  $H_2S$  is 13 to 1, somewhat more favorable than that for high-Btu gas, but the presence of  $COS$  is a serious complication.  $COS$  does not harm SELEXOL Solvent and is absorbed by it, but its solubility is somewhat less than that for  $H_2S$ , which indicates that relatively higher circulation rates will be required. This will cause a greater absorption of  $CO_2$ , leading to a less-rich Claus feed. In short, if  $COS$  becomes the key component, it will be more difficult to produce a satisfactory Claus feed, since the selectivity between  $COS$  and  $CO_2$  is about half that between  $H_2S$  and  $CO_2$ .

Nevertheless, it is possible to meet these requirements with an efficient absorber and some recycling. The simple flowscheme for this process is given in Fig. 2.

If the concentration of each solute can be 0.5 ppm, the degree of  $H_2S$  removal will be 99.9923%, and of  $COS$  removal, 99.23%. If  $COS$  is removed to the required degree,  $H_2S$  will be also, provided that stripping is good enough. Thus, absorption will be controlled by  $COS$  and stripping by  $H_2S$ . The stripping gas is steam, so that the Claus

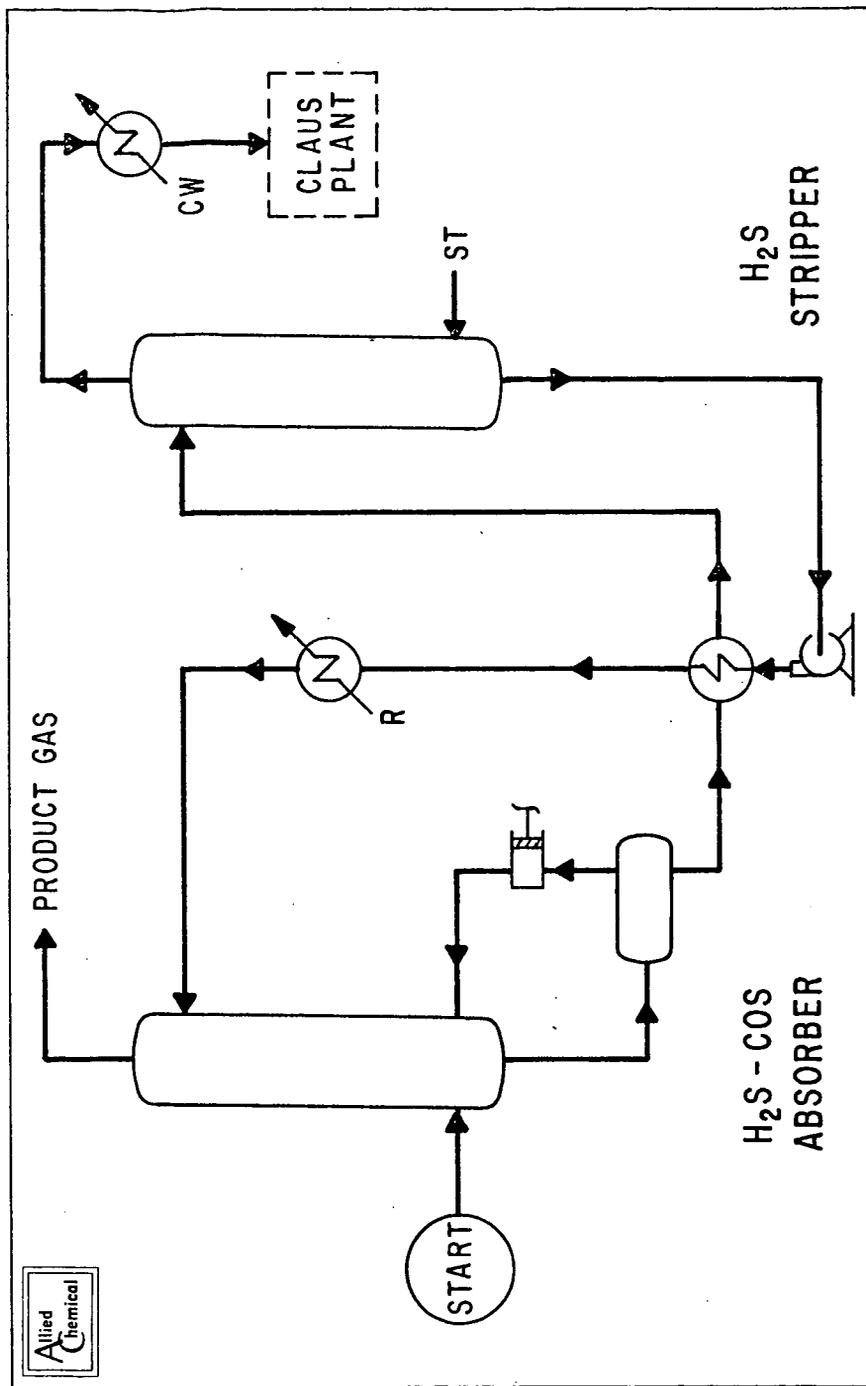


FIG. 2 SELEXOL™ PROCESS FLOW SCHEME FOR LOW-BTU GAS FROM COAL GASIFICATION

gas will consist only of  $H_2S$ ,  $COS$ , and  $CO_2$ . The  $H_2S$ - $COS$  content will be over 15% but under 20% because of the lower selectivity between  $COS$  and  $CO_2$ .

#### Conclusion

The trend of anti-pollution regulations governing synthetic fuel gas plants is toward conversion of almost all sulfur in feedstocks to elemental sulfur. The most reliable and economical conversion plant is the Claus plant, which does, however, need reasonably concentrated feeds for efficient operation. Because of high inherent selectivity for  $H_2S$  and  $COS$  over  $CO_2$ , SELEXOL Solvent can successfully concentrate these sulfur compounds for Claus processing and yet remove them from products sufficiently to satisfy the most stringent requirements.

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