THE REMOVAL OF HYDROGEN SULPHIDE FROM SASOL COAL GASIFICATION OFF-GAS

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SUMMARY

The Sasol Oil-from-Coal plants at Secunda, South Africa are equipped with process units to remove hydrogen sulphide from the coal gasification off-gas to a level which allows the gas to be released to atmosphere. The hydrogen sulphide is produced in the gasification step and removed along with the off-gas during the gas purification stage.

The off-gas flow rate at each of the two Sasol plants comprises approximately 30% of the gas produced from coal gasification and this stream is contacted with the wash solution in the sulphur removal unit to remove in excess of 90% of the hydrogen sulphide in the feed stream. Elemental sulphur is produced in the process as a product.

The process utilised for the absorption of the hydrogen sulphide and subsequent recovery of the sulphur has been jointly developed by Sasol and Linde for this particular application. The process has been successfully developed over a relatively short period and effective removal of the hydrogen sulphide pollutant from the off-gas stream is achieved while reproducing elemental sulphur as a valuable by-product.

INTRODUCTION

The Sasol Secunda complex, consisting of two virtually identical factories (Sasol Two and Sasol Three) is one of the largest petrochemical complexes in the world, comprising an investment of just over US$ 6 000 million (between 1974 and 1982) and covering an area of some 2 000 hecttares.

The Sasol oil-from-coal process (Figure 1) consists of a series of inter-dependent processing units, with Gasification and Synthol forming the most important links. In summary:

- coal is received by conveyor belt from the Mines and sized in a Wet Screening Plant. Coal fines are fed to boilers which supply steam for process operations and for power generation.
- the coarser coal is fed to Lurgi gasifiers, where together with steam and oxygen (the latter produced in an air separation plant) raw gas with an optimum hydrogen/carbon monoxide ratio is formed. The raw gas also contains carbon dioxide, methane, nitrogen, hydrogen sulphide, ammonia, oil and tar.
- the raw gas is cooled to condense an aqueous phase (gas liquor) containing water-soluble substances and crude tar, which are subsequently separated in the Gas Liquor Separation unit. The gas liquor is fed to a Phenosolvan unit where phenols are recovered by liquid-liquid extraction and further treatment of the aqueous effluent produces anhydrous ammonia.
- the cooled gas is then treated in a Rectisol unit, a proprietary Lurgi process for the purification of the raw gas. In this unit, carbon dioxide, hydrogen sulphide and organic sulphur compounds are removed by methanol absorption at sub-zero temperatures and a purified synthesis gas is produced. The off-gas is subsequently routed to the Sulphur Recovery unit before release to atmosphere via the steam plant stack
- the purified synthesis gas is fed to the Synthol unit, a proprietary process, licensed by Sasol and based on the Fischer-Tropsch reaction for conversion of synthesis gas to oil. In this unit, the gas entrains a circulating iron-based catalyst in the reactors and produces a product gas consisitng of hydrocarbons and oxygenated chemicals. This stream is cooled to produce gaseous and liquid hydrocarbons and an aqueous chemicals mixture
- the hydrocarbon liquid is fed to an oil products recovery plant, where a series of oil-refining units produces gasoline and diesel
- the aqueous solution is treated in a chemical products recovery plant, for recovery of alcohols and ketones
- the gaseous uncondensed portion of the Synthol effluent gas is further treated in a cryogenic separation unit. A methane-rich stream is recovered for subsequent reforming to hydrogen and carbon monoxide to provide additional feed for the Synthol process. Ethy-

lene is recovered as such and ethane is cracked to provide additional ethylene. Propylene and LPG are also recovered in the process.

ENVIRONMENTAL ASPECTS OF HYDROGEN SULPHIDE EMISSIONS

Along with a significant amount of heavy industry, the Sasol Secunda plants are located to the east of Johannesburg in a rural inland area of South Africa called the "highveld". As previously stated, the off-gas is released to atmosphere via the steam plant stack. At the final release elevation of about 300 metres, and at the temperature of the steam plant flue gas, the natural atmospheric dispersion was believed to be sufficient to dilute the hydrogen sulphide. The highveld area, however, experiences some unique weather conditions, particularly in winter. At times, in stable conditions with a light easterly wind, the emissions from all the industrial sources can drift in an uneven layer, with little dispersion, the 160 kilometres to the densely populated area around Johannesburg and Pretoria.

Although the threshold limit value (TLV) for hydrogen sulphide is 15 parts per million (eight hour weighted), its presence can be detected by its distinctive and unpleasant odour at levels as low as 20 parts per billion (0,02 parts per million). Therefore, not only is it essential to avoid ground level concentrations approaching the TLV but also it is necessary to avoid the associated unpleasant odour.

A number of hydrogen sulphide measuring stations are located in and around Secunda, with a further station located within the greater Johannesburg area. On occasions, ground level hydrogen sulphide concentrations of about 150 parts per billion have been recorded in the Secunda area, while simultaneously almost as much has been recorded in Johannesburg. Although such occurrences were infrequent, the associated odours were unpleasant.

ORIGINAL PROCESS UNITS FOR HYDROGEN SULPHIDE REMOVAL

Hydrogen sulphide is produced during the coal gasification stage of the Sasol process by the reduction of the sulphur present in the coal and is removed along with the carbon dioxide in the Rectisol unit. This resulting off-gas is routed to a Sulphur Recovery unit where most of the hydrogen sulphide is removed before releasing the carbon dioxide to atmosphere.

Each of the Sulphur Recovery units installed was designed to accept approximatley 500 000 normal cubic metres/hour of off-gas. The Stretford process, a low pressure, liquid phase oxidation process, developed by the British Gas Corporation for the removal of hydrogen sulphide from coke-oven gases, was originally selected as being potentially the most suitable process for these units.

The decision to utilise this process was based upon a detailed study of a number of commercially available processes, although few were applied on a large scale at the time. The first of Sasol's Stretford units was constructed at the Sasol One plant in Sasolburg shortly before the Sasol Two plant at Secunda was built. When the Sasol Two project was announced in 1974, construction of the Stretford unit at Sasolburg had only just begun. Consequently, the design of the Sasol Two unit was delayed until some operating experience could be gained at Sasol One. In 1977, it was decided to build a Stretford unit at Sasol Two for the removal of hydrogen sulphide, although only very limited experience had been gained on Sasol off-gas at Sasol One.

Operation of the unit at Sasol One was initially delayed and later severely affected by a number of problems both related and unrelated to the process. Since the Sasol Two plant was similarly designed, but significantly larger, it was felt that the risks involved in commissioning such a huge plant were too great.

In 1979, when construction of Sasol Two was underway, permission was granted to delay the commissioning of the units at Secunda, and to either seek solutions to the problems or find an alternate process that would be more compatible with the constraints imposed by Sasol's off-gas, by zero effluent design and by physical plant size. Additionally, any alternate process had to be easily accommodated within the physical plant already constructed, or under construction, to allow expedient commissioning.

ALTERNATIVE PROCESSES

Investigations were begun immediately to develop solutions or to find a process that would be suitable, and a number of commercially available processes were considered. Pilot scale tests were carried out to determine compatability with Sasol off-gas with a view to full scale tests on the Sasol One unit.

Finally, alternatives to the chemistry of the process appeared to offer the most promising options. One such process, developed over an eight year period in the United States of America, was first tested on simulated Sasol gas in a pilot plant in the USA and as the results were encouraging, it was decided to demonstrate the process on a commercial scale in the Sasolburg plant. The test was generally successful but with some unexpected problems. It was established that the absorption solution would be very expensive and extensive modifications and additions would have to be made to the existing plant. At that stage, however a more attractive option became available.

In 1982, while Sasol was investigating various processes, Linde AG, TVT Division, Munich, who had handled the design of the Sulphur Recovery units at Secunda, began laboratory work on a new solution that could be utilised by Sasol. Sasol became involved in Linde's development work which eventually led to a new hydrogen sulphide absorption solution, later to be named "Sulfolin". The Sulfolin solution, as demonstrated in the laboratory, displayed a number of advantages, including:

- high activity
- chemical stability
- low by-product formation
- non-corrosive
- low cost.

By early 1983, joint development of the Sulfolin solution by Sasol and Linde had progressed to such an extent that there was sufficient confidence to construct a pilot plant at Secunda to operate on Sasol Two Rectisol off-gas. The pilot plant, treating 100 normal cubic metres/hour, was commissioned in late 1983 and the expectations for the Sulfolin solution were confirmed within a six month period.

By early 1984 the research work was complete and Sasol was able to proceed with the commissioning of the Sulphur Recovery units at Secunda utilising the Sulfolin process and thereby make a contribution in reducing the hydrogen sulphide odours. To minimise the risk, it was decided to conduct a commercial demonstration test to one of the four virtually identical "phases" installed. Such a decision was not without its own risk, as can be appreciated from the large scale-up factor of approximately 2 500 (based on gas through-puts).

FULL SCALE APPLICATION OF THE SULFOLIN PROCESS

Since Sulfolin was essentially a new chemical solution operating on principles compatible with the original process, it was possible to accommodate the Sulfolin process in the existing physical plant at Secunda. These plants are of a considerable size as can be appreciated from the following paragraphs which provide a brief process description of one phase.

A stream of approximately 250 000 normal cubic metres/hour of Rectisol off-gas enters the Sulphur Recovery unit in a 1 500 millimetre diameter line. Since the coal utilised at Secunda is low in sulphur the off gas consists predominantly of carbon dioxide. The first stage of the process (Figure 2) occurs in the absorption section where the gas is contacted with the Sulfolin liquor in two multi-stage venturi absorbers to remove most of the hydrogen sulphide from the off-gas. Each of the two absorbers is approximately 15 metres in height and nearly 6 metres in diameter. Venturi absorbers were chosen because blockage by solid sulphur was considered likely in a packed tower absorber, and because short contact time absorption devices appeared more suitable for the service. In addition, the height of the equivalent packed column would have been in the order of 75 metres. After the absorption section the cleaned off-gas is discharged to atmosphere via the steam plant stack.

The Sulfolin liquor, containing elemental sulphur and hydrogen sulphide ions flows into two reaction tanks where the formation of solid sulphur continues. The contents of the reaction tanks are continuously stirred to prevent settling of sulphur. The liquor, containing the suspended sulphur, flows from the reaction tanks into the first of two oxidisers in series. The oxidisers serve the dual purposes of regenerating the Sulfolin liquor for re-circulation to the venturi absorbers and producing a sulphur-rich froth by flotation using compressed air. The oxidised Sulfolin liquor flows from the second oxidiser into a surge tank before it is recirculated to the venturi absorbers.

The sulphur-rich froth flows from the top of the second oxidiser to three slurry tanks, each feeding a decanting centrifuge. The centrifuge produces an enriched sulphur cake and clean liquor for recycle to the surge tank. The enriched sulphur cake is pumped and heated by injecting steam to produce a mixture of molten sulphur and liquor which is separated by gravity in a separating vessel. The resulting separated molten sulphur is stored in an underground storage facility.

The liquid sulphur is transported by road tanker to a granulation plant serving both Sasol Two and Sasol Three where a prilled sulphur product is produced. The two Sulphur Recovery units are located some 2.5 kilometres apart and each is about 3 kilometres from the granulation plant. It was decided that the pumping of liquid sulphur over these distances was not practical and therefore road tankers were chosen. A granulation plant is installed because the South African market demands only a granulated product.

As an overall indication of the plant size it is interesting to note that the total liquid solution inventory in each of the Sulphur Recovery units is about 28 000 cubic metres. Additionally, each of the two units consumes about 16 MW of electricity, equivalent to the electricity usage of a town with a population of about 30 000.

ASPECTS OF THE COMMERCIAL DEMONSTRATION TEST RUN

Since the scale-up from the pilot plant to full scale involved a factor of approximately 2 500 the associated risks were considerable.

The commercial demonstration run was commenced in October 1984 and initially operated successfully. The size of the scale-up resulted in a number of unexpected results. After about seven days operation considerable vibration and turbulence developed in both oxidisers and the unit was subsequently shut down. On inspection it was discovered that severe mechanical damage had occurred inside the oxidisers. Investigations, including the construction of a large perspex model of an oxidiser revealed that the force of the incoming liquor had resulted in excitation to the natural frequency of the liquid in the tank with consequent wave formation. The physical characteristics of the air distribution system were subsequently completely redesigned, and following further pilot plant tests the new system was installed in the oxidisers.

The modifications to the air distribution system required the original oxidiser internals to be completely removed and replaced. Since this work was of considerable proportions, due to the physical plant size, a restart to the test run was not possible until June 1985. The re-designed system operated as predicted and no vibrations were detected.

A number of other smaller problems have occurred, all of which have been largley overcome. Some of these have been

- lower than expected venturi absorption efficiency, improved by modifications to the absorbers
- Lower than expected sulphur removal efficiency of centrifugal decanters, improved by modifications to the machine internals
- local carbon dioxide pollution around the oxidisers, especially during winter, greatly improved by the installation of reducers on the oxidiser breather stacks to increase the velocity and the dispersion.

The commercial demonstration test of the Sulfolin process was officially and successfully completed in October 1985. The results to date have confirmed that the chemical stability is good and the by-product formation (sodium sulphate and sodium thiosulphate) is essentially zero. Additionally, a number of modifications were identified that were required to achieve a successful unit commissioning. Following the completion of the test run, immediate action was taken to modify and commission the remaining Sulphur Recovery facilities at Secunda. Current plans indicate that the remaining three phases of the Sasol Two and Sasol Three Sulphur Recovery units will be fully operational by the third quarter of 1986.

CONCLUSIONS

Sasol was originally faced with a particularly difficult problem in that its off-gas, containing less than 3% hydrogen sulphide was not compatible with the original process selected. Quite clearly, the composition of this stream and the size of the Sasol Two and Sasol Three plants made the choice of an alternative process just as difficult. The development of a "custom" process has turned out to be the best solution in Sasol's case.

The Sulfolin process has been developed from Linde's laboratory scale to full scale in the short period of approximately three years. This has been made possible by a continuous effort by Sasol, including the expenditure of significant amounts of capital to effectively remove the hydrogen sulphide from the off-gas, exemplifying Sasol's continuing concern for the environment.

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The result of three years development is the successful operation of a plant that removes approximately 90% of the hydrogen sulphide in the feed gas. This, however, is not the end of the development. As part of an on-going programme of monitoring the operation and performance of the plant, investigations are continuing into greatly improving the hydrogen sulphide removal efficiency. The Sulfolin process is in fact still being developed on a full scale basis. The advantage of this is that the lessons learned during the operation of the first phase can be applied to the remaining three phases, either in the form of modifications that can be implemented before their commissioning or by operational changes.

It is Sasol's objective to have all of the hydrogen sulphide removal facilites fully and efficiently in operation by the third quarter in 1986 and thereby make a valuable contribution to the environment.

it is also interesting to note that although the Sulphur Recovery units were designed and installed purely for environmental reasons, these units will make a valuable contribution to the income of the Sasol plants as a result of the present world sulphur price.