

https://dspace.org/

Sulphur removal from coal or from products: is prevention better than cure? - a techno-economic review

Koper, Edward Ludovicus

2009-07-01T12:50:49Z
http://hdl.handle.net/10539/7060

Downloaded from a DSpace repository. https://dspace.org/

3 BACKGROUND

As mentioned in Chapter 2, the challenge addressed in this thesis is the evaluation of the benefits of coal beneficiation as an alternative to gas treatment options in the reduction of sulphur emissions from the gas production sections of the Sasol Synfuel complex, considering the impact on the whole Secunda complex. For this to be possible, it is required to have a better understanding of the processes within the Gas Production section of Sasol Synfuel, as well as the coal used as feed to this section.

Various solutions are available to address the sulphur in the coal or in the gasification raw gas. The most suitable solution depends on the way in which the sulphur species are present in the process stream, the process conditions and the extent to which the process stream containing the sulphur species is allowed to physically change.

The following sections first supply background to the origin of sulphur in the process streams. In the next chapter, various process alternatives to address the sulphur in the gas stream or the sulphur in the coal will be reviewed.

3.1 The Origin Of Sulphur In Coal

The origin of coal is very well described by many authors in the literature and is summarized to the extent relevant to the context of this thesis in paragraph 1.2 and will not be repeated here. The coal reserves for the Sasol Secunda complex are a given and their nature and character cannot be retrospectively altered.

Sulphur is recognized as one of the major impurities in coal, and occurs in coal in various forms and results from various sources [Heras [(4)]]. The most important form is sulphide, mainly as pyrite, FeS_2. Other forms are organic sulphur (captured in the vegetation during the life of the plants) and sulphur as sulphates. Sulphatic sulphur occurs in small amounts, often formed as the result of the oxidation of other sulphur components in the coal originating from plant material or even from pyrite [Ryan [(5)]].
Elemental sulphur, from geothermal activities, can also occur but is very rare in the Secunda coalfield.

3.1.1 Pyrite

A suggested process for the formation of pyrite is described in figure 3.1 [after Press and Siever [(6)]]. Decayed organisms are converted together with sulphates in seawater by

sulphur reducing bacteria *Desulphovibrio desulphuricans* producing hydrogen sulphide dissolved in the water and carbon dioxide. The hydrogen sulphide combines with iron oxides from sediments and dissociated clays to form iron sulphide, which precipitates. Over time and with burial, the iron sulphide re-crystallises as pyrite, FeS_2, in cubes, nodules, or finely dispersed particles.

The influence of acidity (pH) and the presence of bacteria are important for the formation of pyrite [Ryan [(5)]]. The pH typically is between 4.5 and 7, and the bacteria are anaerobic types. Hence, the turbulence of the basin wherein the bacterial conversion of iron and sulphates takes place is of importance: the more turbulence, the more oxygen, and the lower the bacterial activity. Typically, the inflow of new water into the basins should be limited to a few times per year to maintain an anaerobic environment, and still supply sufficient sulphates to the bacteria for the conversion. The sulphates are carried with the seawater, averaging approximately 2700 mg/l SO_4 (in comparison to fresh water in rivers at approximately 8 mg/l) [Pennsylvania EPA [(7)]]. To satisfy these conditions it can be suggested that a delta is formed at the end of a fluvial system, with a bank on the seaside preventing continuous ingress of seawater but low enough to be overrun by the waves during spring tides [Press, Siever [(6)]].

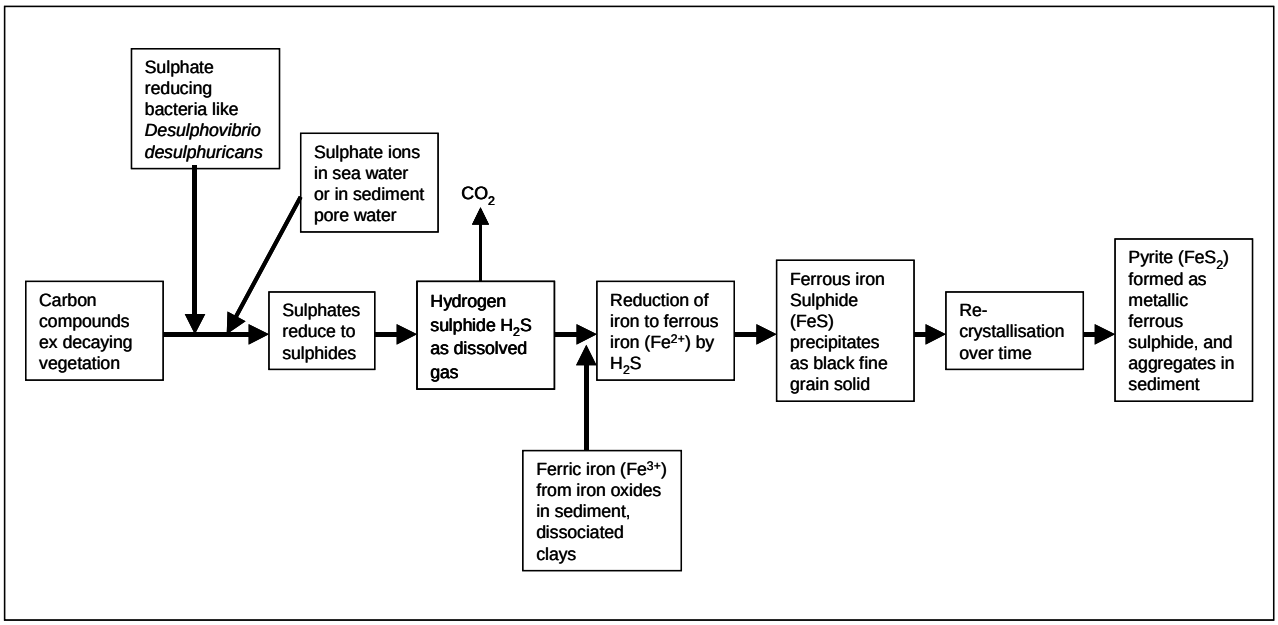


Figure 3.1 Formation of pyrite through anaerobic bacterial conversion of sulphates

References are made to studies performed by Roberts in 1988 on South African coals where the seawater influence was not that strong [Roberts [(8)]]. The studies suggest a good correlation between high vitrinite and higher sulphur / pyrite contents on the one hand, and high inertinite and lower sulphur / pyrite content on the other. This would

suggest that the higher water table, favouring formation of vitrinite under low oxygen, high pH conditions would also favour the formation of sulphur / pyrite components. The lower water table conditions would have a low pH and high bioactivity, favouring inertinite.

The formation of framboidal pyrite (spherical clusters of very fine pyrite crystals of sizes smaller than 2 µm, named after the French word for raspberries) is usually through the bacterial reduction of sulphur in the vegetation and is formed at the beginning of the metamorphosis in the peat swamps. Its formation appears not to be dependent on the supply of sulphates from seawater [Ryan [5]]. Framboidal pyrite can also be formed as the result of the reduction of sulphates produced through the oxidation of sulphur components in the coal after the coal seam was formed. Cracks in the coal seam would allow water to enter the coal seam and start the oxidation process. The size of the framboids is so small, that coal needs to be reduced to very small sizes to liberate this form of pyrite. Microscopic investigations by Greer [9] indicate that framboids may form assemblies or clusters and interlink with other pyrite over a large-size range up to centimetres in width or even greater.

Sulphur-34 isotope analysis indicates the principal source of sulphur in low-sulphur coal is from bacterial conversion of sulphur in plant material, and that the higher sulphur coals obtained the sulphur through bacterial conversion of seawater sulphates [Gammidge [10], Dai [11], Roth [12], Deer [13]].

Figures 3.2, 3.3 and 3.4 depict pyrite occurrences in Secunda coal.

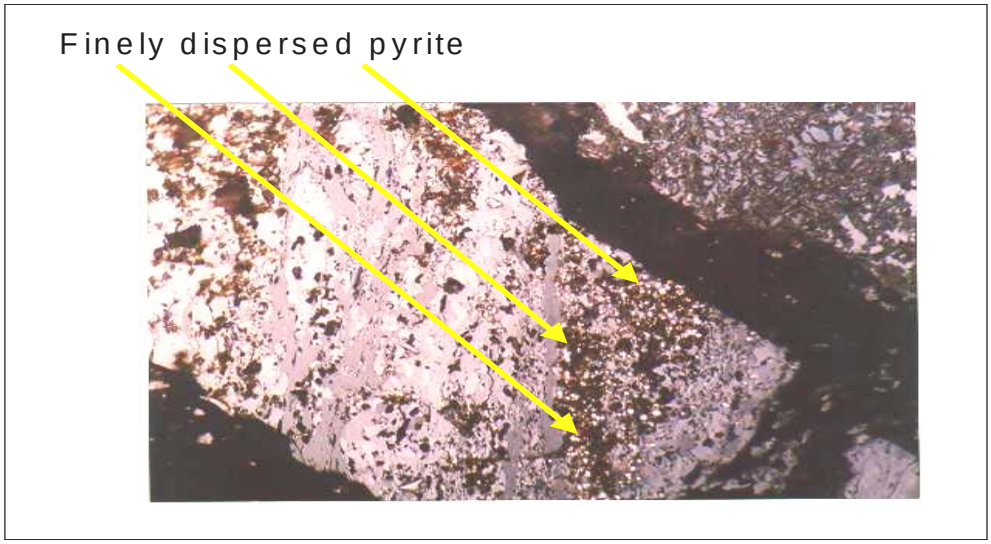


Figure 3.2 Finely dispersed pyrite in Secunda coal

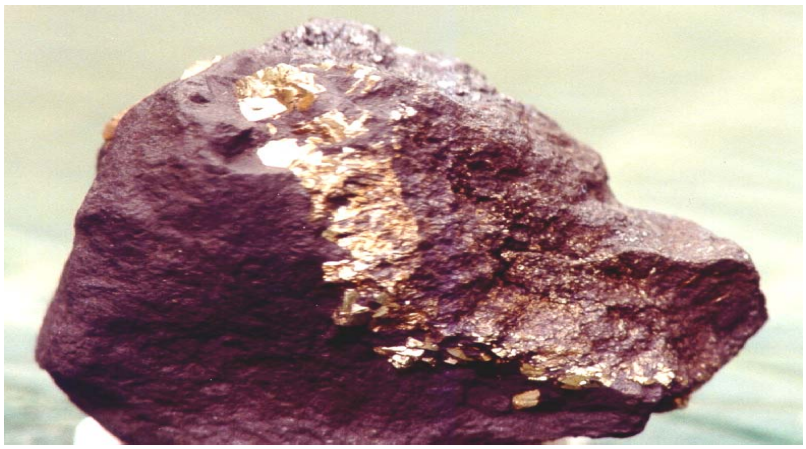


Figure 3.3 Pyrite vein in Secunda coal



Figure 3.4 Discrete pyrite nodule in Secunda coal (torbanite)

Pyrite is by far the most common sulphur specie in the Secunda coal deposit. Its concentration varies from size fraction to size fraction and with density fraction. Micron sized pyrite particles can be observed in microscope photos, and pyrite nodules of millimetre and even centimetres size dimensions have been identified in coal lumps in the gasification feed material.

Petrographic analyses of the Secunda coal indicate that pyrite can be present in various modes: fine grained, nodular, framboidal, cell replacement and fissure/crack filling [Keyser [(14)]].

3.1.2 Organic sulphur

Sulphur components are also present in the vegetation itself, since minerals were absorbed into the plant's structure to allow it to grow. Organically bound sulphur is present in amongst others thio-compounds like thiophenes and mercaptans, aromatic sulphides and aliphatic disulphides [van Krevelen [(15)], Ryan [(5)]. It is suggested that these can occur in the ration 50:30:20 [Attar [(16)]. Van Krevelen [(17)] further remarks that the organic sulphur probably almost completely occurs in heterocyclic (aromatic) structures like condensed thiophenes.

The higher the rank of the coal, the more the organic sulphur will be present in aromatic structures since coal tends to form more ring compounds from the aliphatic chains when progressing towards a graphite like structure. Organic sulphur is usually distributed in a uniform manner throughout the organic material matrix constituting the particular maceral in the coal, and can therefore not be isolated from coal without changing its organostructure. This is why organic sulphur is the most difficult form of sulphur to remove from coal [Edgar [(18)]].

Organic sulphur does not only denote sulphur originating from vegetation, but also sulphur from sulphates in water which was first reduced to H_2S and then reacted and became included in the coal molecules (rather than forming pyrite).

3.1.3 Sulphur as sulphates

Sulphates are the result of the oxidation of sulphur. Pyrites will oxidise when exposed to heat and water and form sulphuric acid, which in turn will react with minerals and clays available in the vicinity to form sulphates. The most common one is calcium sulphate.
Similarly, organic sulphur will form sulphates when oxidised. Sulphates can be deposited in the cracks of the coal seam during the formation of the seam and afterwards, resulting from the precipitation of dissolved mineral salts from the water seeping into the cracks.

Of all three forms of sulphur, sulphur as sulphates is by far the least in the Secunda coal, and the concentration remains more or less constant over size and density fractions.

The effect of sulphur and sulphur species on the Sasol processes are very well studied with respect to the effect sulphur may have on the Fischer-Tropsch (Synthol) processes. Sufficient effort and engineering has always been spent on the removal of sulphur related species from the feed gas to the Synthol reactors, and the challenges to the Rectisol raw

gas purification system were more of a volume (throughput) nature than of product quality (sulphur content) nature. This tempered the urge to evaluate methods to reduce the sulphur content in the feed material (coal) to the Sasol system as well as the research into the coal itself with respect to sulphur species, species distribution, mineral liberation, etc. Complex throughput has increased however, and with that the demands on the gas purification and sulphur recovery systems to the point that coal preparation to reduce sulphur intake into the complex may now be considered as an alternative method to ensure correct quality pure gas to the Synthol units and reduced load on the sulphur recovery unit.

To be able to evaluate coal preparation as an alternative to reduce sulphur intake into the complex, proper coal analyses with respect to sulphur and sulphur species are required. These were not available initially, and the necessary sampling campaigns over a sufficiently long period had to be performed to establish relevant information. More about this in Chapter 7.

The gasifiers do not use all the coal fed to the Sasol Synfuel complex. Approximately one third of the coal, predominantly the minus 5 mm fraction, is fed to the pulverised fuel boilers for the production of steam. The steam produced is used as part of the agent driving the gasification processes in the gasifiers, the gas reformers as well as the driver for the turbo-generators for the production of oxygen and electricity for internal consumption and critical power back-up.

Most of the sulphur in the coal fed to the steam generation units is converted into sulphur dioxide in the combustion process. The sulphur dioxide remains in the flue gas of the boilers and is routed to atmosphere via the flue gas chimneys.

There are environmental aspects to the release of sulphur dioxide from steam / power generation operations, mainly the contribution of these releases to the production of acid rain and consequent acidification of lakes, agricultural land and forests. Although this is a serious issue on itself, it will not be addressed further in this research project. As mentioned, this thesis focuses on the synthesis gas production processes in the Sasol Synfuel complex in Secunda.

3.2 The Origin Of Sulphur In The Gas Stream

The Sasol Synfuel complex converts carbon in coal to carbon in value added products through the application of Fischer Tropsch (FT) chemistry on a mixture of predominantly hydrogen and carbon monoxide. The first step in this process is the conversion of carbon in coal to carbon in gaseous form (raw gas), followed by the purification of this raw gas to remove components harmful to the FT process or diluting the useful components. The conversion step is performed in Sasol-Lurgi Fixed Bed Dry Bottom gasifiers.

The Sasol-Lurgi gasifier is a fixed bed dry bottom gasifier, meaning that the ash is removed dry not via a slag bath, operating at approximately 30 bar and mild gasification temperatures (800 – 1300 °C). Figure 3.5 shows the gasifier and it various process zones.

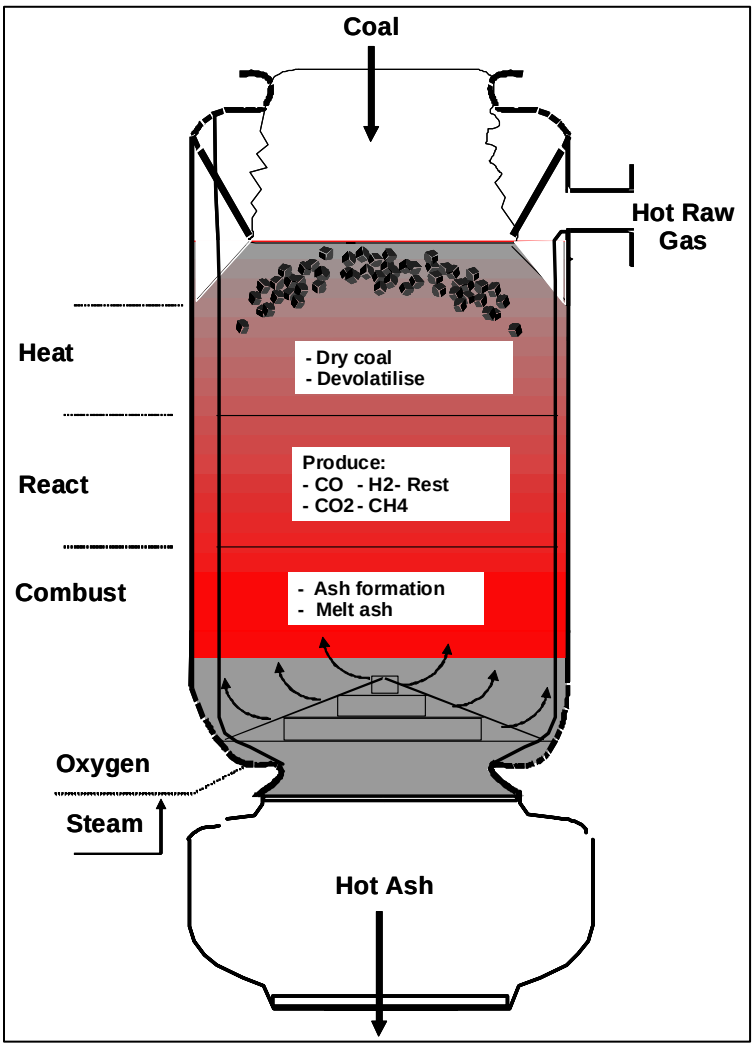


Figure 3.5 Sasol-Lurgi Fixed Bed Dry Bottom gasifier

Relatively coarse coal (± 5 to 100 mm) is fed from the coalbunkers on top of the gasifier into a coal lock. After pressurising the coal lock, the coal is discharged into the gasifier. The temperature in the very top part of the gasifier is approximately 120 °C, increasing rapidly to over 250 °C and the moisture on the coal starts evaporating. The coal heats up as it moves down through the gasifier (ash is turned out at the bottom by a rotating grate, moving the ash into an ash lock and creating a downward movement for the coal bed in the gasifier). The temperature of the coal particle will increase and volatile components of the coal are driven of. These components comprise methane, light hydrocarbons and, at higher temperatures, crystal water. Further down in the gasifier the particles become so hot that the volatile components still escaping from the coal particles are cracked into smaller hydrocarbons and radicals. These radicals can react with the hydrogen and carbon monoxide / carbon dioxide molecules and other radicals. Even further down the devolatilised coal, red-hot char by now, reacts with steam and oxygen to form carbon monoxide, carbon dioxide and methane in the gasification zone.
The combustion zone, the lowest and hottest reaction zone in the gasifier, is the zone where carbon is combusted with oxygen to release the energy from the coal. This exothermal reaction zone supplies all the heat for the endothermal gasification and reduction processes higher up in the gasifier. This zone experiences the highest temperatures in the gasifier, up to 1400 °C. The minerals in the coal are oxidized, and some degree of ash softening takes place to form ash clinkers. The burnt-out coal (essentially reduced to a mineral oxide matrix) leaves the gasifier as a semi-agglomerated ash.

At the gas outlet, the raw gas components leave the gasifier at a temperature of approximately 550 °C. Most of the raw gas is hydrogen (approximately 40 %), followed by carbon dioxide (± 27%), carbon monoxide (± 21%), methane (± 9%), hydrogen sulphide, and argon from the oxygen (together ± 3%).

The textbook version of the Lurgi gasifier process theory depicts these zones as distinct horizontal planes. Practice however shows that the zones are all but horizontal. The transitions from zone to zone are still there, but they can be positioned anywhere in the top two-thirds of the gasifier, with a sloping plane connecting the various active points. These planes move up and down with time, and are strongly influenced by coal particle size distribution, reagent (steam and oxygen) distribution and in general the variation in physical and chemical coal characteristics from point to point in the coal bed. The composition of the raw gas produced in the gasifier varies therefore from point to point. Not only the percentage of desired components – hydrogen and carbon monoxide – varies, but also that of the other components including hydrogen sulphide.

The processes would benefit from a mixture of coal fed to the gasifier that is as homogeneous as could be in all respects: size distribution, reactivity, mineral composition, petrography etc. Although attempts are made to blend coal of the different mines, and some homogenisation does take place on the stockpiles, the material fed to the gasifiers still varies a lot from hour to hour, and most certainly between coal lock fillings. Since the movement of material through the gasifier is relatively slow (one batch of coal stays approximately 1.5 hours in the gasifier), a variation in coal quality can influence operating conditions for a considerable period. If a means could be found to reduce the variation in coal quality characteristics, this would certainly be beneficial for the process.

Figure 3.6 is a process block flow diagram depicting the Gas Production section of the Sasol Synfuel process in Secunda. After the raw gas leaves the gasifier, a scrubbing and cooling step follows. In this step, most of the solids entrained from the gasifier are removed with an internal water stream, and the gas is cooled to below 200 °C. The drop in temperature results in the condensing of higher (longer chain length) hydrocarbons: oil and tar. In these hydrocarbons, certain sulphur compounds are also present. Further cooling takes place *en-route* to the Gas Purification section and in each cooling step additional hydrocarbon condensates are formed. The raw gas stream stays water saturated, and all the excess water condenses-out in each cooling step. The water, "gas-liquor", also contains some of the sulphur compounds. The tar and oily condensates as well as the water are collected in a gas liquor separation unit. In this unit, the hydrocarbon phase is separated from the water phase. The hydrocarbons are routed to the Refinery section for further processing into fuels. The water phase is routed to a work-up section for the recovery of ammonia and phenols, and thereafter to a water recovery unit to produce process cooling water.

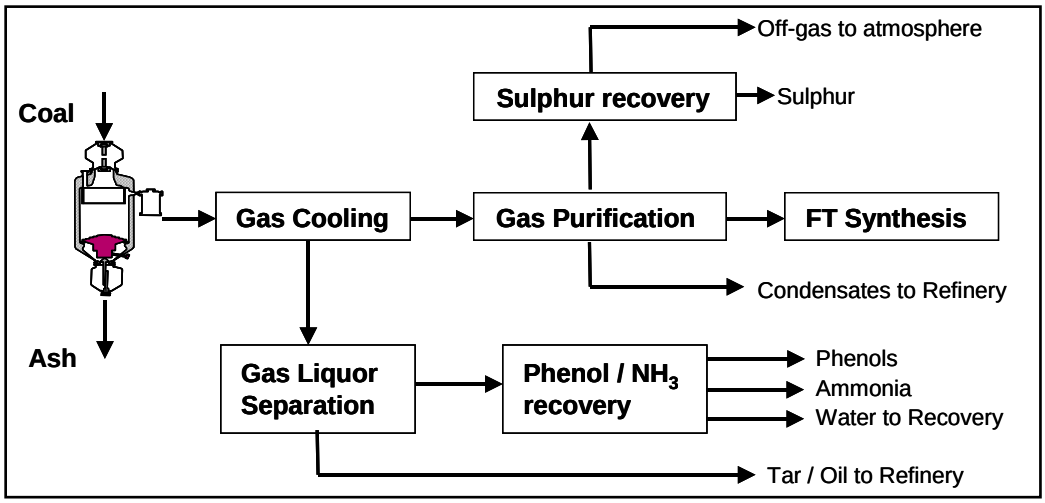


Figure 3.6 Sasol Synfuel Secunda gas production block flow diagram

The cold raw gas enters the Gas Purification section through a series of heat exchangers where the remaining water and hydrocarbons are condensed out of the raw gas stream to prevent blockages in the gas purification process equipment. The water stream is returned to the gas liquor separation plant. A naphtha stream consisting of hydrocarbons, some of which contain sulphur compounds, is sent to the Refining units for processing to fuel products.

The Gas Purification process is a Lurgi / Linde Rectisol process, utilizing very cold methanol to absorb the sulphur components in the raw gas as well as the carbon dioxide [Kauf [19]], Keresteciogl [20]].
The removal is very effective and the sulphur content of the pure gas stream is in the low ppm levels, well within the quality requirements for the synthesis units. The sulphur and carbon dioxide laden methanol is expanded in a vacuum column. This releases the carbon dioxide and the sulphur components, and provides most of the cooling required for making the (now warmed up) methanol cold enough again to be returned to the wash column.
Figure 3.7 is shows the Rectisol process.

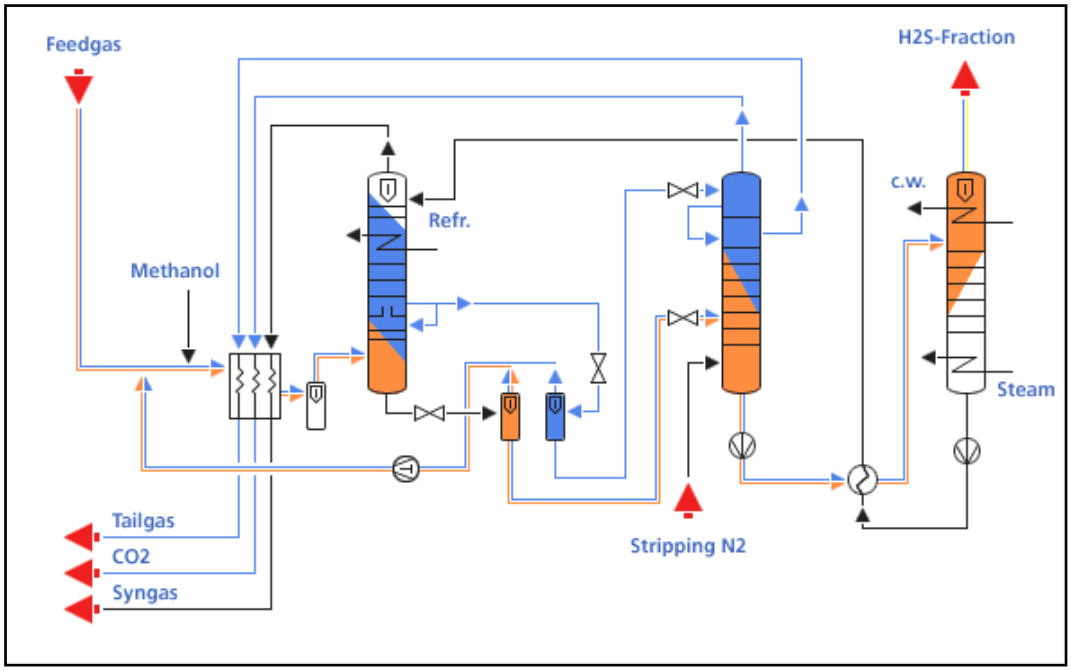


Figure 3.7 Process diagram of the Lurgi/Linde Rectisol process

The Rectisol off-gasses are mainly carbon dioxide, hydrogen sulphide and mercaptans, but also contain some carbon monoxide, hydrogen and methane. This off-gas stream is routed to the Sulphur Recovery plant for the recovery of elemental sulphur. Sulphur

recovery is achieved through a vanadium-based redox process, converting the hydrogen sulphide into elemental sulphur, which is sold.
The remaining sulphur-lean off-gas is routed to atmosphere via the Steam Plant flue gas chimneys, and released more than 250 meter above ground level for safe dispersion.

On a typical day, the 80 gasifiers in Secunda consume approximately 65 000 ton of coal (2600 ton per hour), and convert that to approximately 4.5 million m^3_n raw gas per hour, with a sulphur content (as H_2S) of ± 1.0-1.5 volume %. The sulphur recovery units have been able to recover as much as 410 ton elemental sulphur per day. From sulphur balances over the Gas Production section, it appears that most of the sulphur indeed ends up via the raw gas into the Rectisol off-gas.

Table 3.1 Distribution of sulphur over process streams

Stream	**%**
Sulphur in raw gas	73-83
Sulphur in ash	12-18
Sulphur in gas liquor	4-6
Sulphur in tar and oil	1-3
Total sulphur (incoming in coal to gasifiers)	100

The above descriptions of the Sasol gas production process identify a few process-engineering points which need to be considered when evaluating the various technology options to prevent sulphur from entering the process or the handling of the sulphur once in the raw gas stream:

- The gasifiers consume a large amount of coal per time unit. This impacts the size and cost of any coal handling process considered.
- There is mechanical handling of coal and ash.
- The gasifiers work on coarse coal, minimum size approximately 5 mm, top size approximately 100 mm.
- Homogeneous coal would be preferred, with very low variation in coal quality, from coal lock filling to coal lock filling.
- No coal beneficiation currently exists.
- A large volume of raw gas is produced. This impacts on the size and cost of the gas treatment units.
- There is a lot of Rectisol off-gas , and the stream is carbon dioxide rich.
- The quality of the pure gas to the synthesis units is most important and may not be compromised.
- A sulphur recovery process unit already exists.