The Zero-residue Refinery

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1 Introduction

Refineries world-wide are being subjected to increasing pressures both legislative and economic. The effects of the Clean Air Act (CAA) in the United States of America are well documented. In Europe increasing environmental legislation is making itself felt both in refinery operation and in terms of product quality. The former is governed by the requirements of the EU Large Combustion Plant Directive or more stringent national regulations. The latter is dictated by the EU Directive EN 228 requiring a reduction of sulphur in diesel motor fuels to 0.05% S by 1996 and in heating oils to 0.1% S by 1999.

Simultaneously to these legislative pressures there is a medium-term pressure to reduce the low-sulphur crude intake because of declining availability and an increasing cost differential compared with high-sulphur crudes.

Various schemes including either coking or residue gasification have been proposed to cope with these pressures. Realization that coke disposal is becoming increasingly difficult has led to wider application of residue gasification. Four existing refineries in Germany already employ the Shell Gasification Process (SGP) for residue utilization. World-wide four plants are currently under construction including a major revamp at SHELL's own Pernis Refinery near Rotterdam. This paper discusses the integration of the SHELL Gasification Process into the refinery flow scheme in the development of a reduced-residue or even zero-residue refinery in general terms, but includes reference to this latter project as a source of practical examples.

2 SGP in the Refinery Flowsheet

Before entering into a detailed description of the gasification and gas treating technologies, it is necessary review how they fit into the overall picture of the refinery flow sheet.

Figure 1 provides a very simplified view of a refinery flow sheet after the implementation of a combined hydrocracker and SGP project.

The overall project includes the construction of a new hydrocracker (HCU) and the residue gasification unit for the production of hydrogen and sulphur-free fuel gas which will be fed to a gas turbine which forms the heart of a combined cycle co-generation plant. Additionally, the project would include a new amine treating and Claus units.

Feedstock Type		**Visbreaker Residue**	**Propane Asphalt**
Elementary Analysis			
C	[wt%]	85.42	84.37
H	[wt%]	9.93	9.67
S	[wt%]	4.00	5.01
N	[wt%]	0.30	0.52
O	[wt%]	0.20	0.35
Ash	[wt%]	0.15	0.08
		100.00	100.00
Vanadium	[ppmw]	270	300
Nickel	[ppmw]	120	75
Sodium	[ppmw]	30	30
Viscosity (100 °C)	[cSt]	10 000	2 000
Density (15 °C)	[g/cm^3]	1.10	1.07

Table 1: Typical SGP Feedstocks

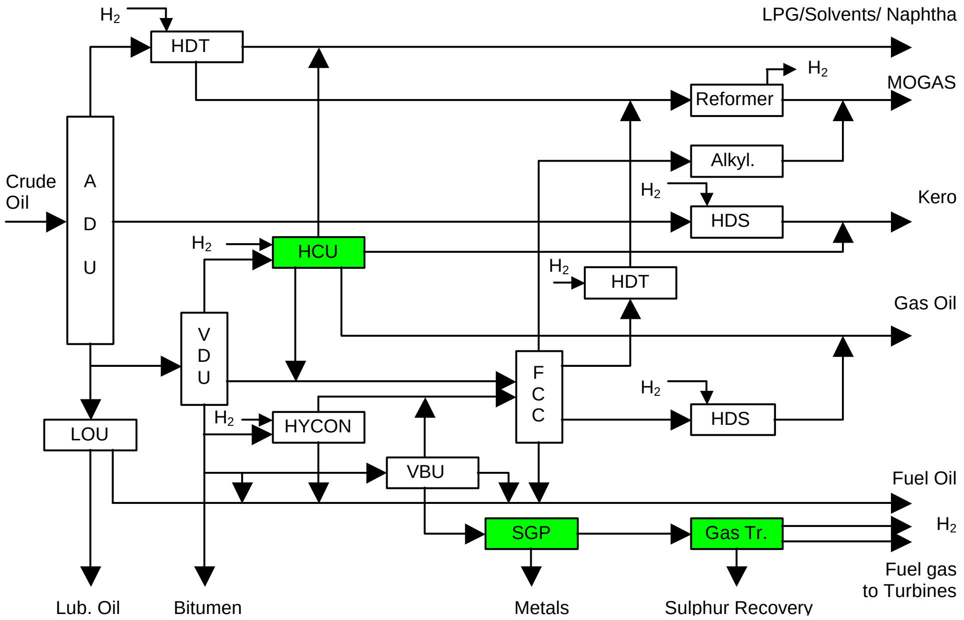

Figure 1: SGP in the Refinery Environment

The feedstock for the SGP unit is a heavy, vacuum-flashed cracked residue from an existing visbreaker unit (VBU). This material is typically characterized by high viscosity and high metal contents. Typical values experienced in operating SGP units are shown in Table 1.

The product hydrogen would be primarily aimed at supplying the hydrocracker. Sufficient flexibility can, however, be built into the gas treatment facilities to accommodate alternative scenarios in the overall hydrogen refinery balance and produce methanol for MTBE production or other uses.

3 Process selection

3.1.1 General

Process selection for a multiproduct gasification unit into which considerable flexibility is specified can be a complex undertaking and it is perhaps useful to discuss some of the key decisions in building up the block flow scheme for the SGP-based hydrogen and power plant (SGHP) as the combined SGP and gas treatment facilities have become known. In essence it becomes a matter of reconciling the optimum selections between the hydrogen plant and the power plant.

3.1.2 Hydrogen

Before looking at internal aspects of the SGHP, however, it is necessary to define the quality of the hydrogen product. Many hydrocracking processes will accept a 98% H_2 purity, which can be produced by the traditional shift, CO_2 removal and methanation route. A number of processes do, however, require higher purities of 99% H_2 or higher, in which case the final purification step will have to be pressure swing adsorption (PSA). The higher purity is, however, achieved at the cost of a lower hydrogen yield (about 85%- 90% instead of 98%) and the production of a relatively large quantity of low pressure, low BTU fuel gas which one may or may not be able to accommodate in the refinery fuel gas balance. It is important in this context to review the hydrogen purity specification carefully with the hydrocracker requirements, since all too often a purity of > 99.5% is specified on the basis of the economics of the conversion unit alone, or on the assumption that hydrogen will be generated from a steam reformer which can accommodate the PSA tail gas internally, without reference to the economics of the overall configuration.

3.1.3 Gasification

When looking at gasification schemes, two alternatives for raw gas cooling are regularly reviewed - waste heat boiler and quench. A second aspect to consider is a decision on the number of trains. Key priorities are reliability and efficiency.

The use of a waste heat boiler for optimum heat recovery can achieve a substantial efficiency improvement on a stand-alone IGCC when compared with a quench unit. On a large plant, say one the size of Pernis, a payout time for the differential investment is, under normal circumstances in the order of 2 years.

The reliability of the SGP waste heat boilers is well documented in over 150 units already in operation, some of which take a feed similar or even heavier than that typically available in modern refineries. For example, here in Germany one operator regularly reports availabilities in the 98% range, year after year.

Train-sizing is usually determined by the requirements of flexibility and operability. In Pernis it was decided to go for three trains. Under normal three train operation, the syngas in excess of the requirement for hydrogen production is used as gas turbine fuel. In case of outage of one gasifier, the hydrogen requirement for the HCU can be delivered from two gasifier trains.

3.1.4 Desulphurization

On a stand-alone IGCC, LURGI's standard desulphurization process selection would be Purisol combined with an oxygen Claus plant, as is being installed for a residue gasification project at Sannazzaro in Italy. This physical washing system has a number of advantages, in particular its high selectivity for H_2S versus CO_2, its ability to absorb a substantial proportion of COS from the raw gas so that the use of an expensive COS hydrolysis stage before the wash is not always necessary and its use of flash regeneration, which provides an important operating cost advantage compared with chemical solvents using hot regeneration.

However, in a project where under normal operation two-thirds of the gas would be used for hydrogen production, it is not a foregone conclusion that the stand-alone IGCC solution represents an overall optimum. Indeed, this is not the case. Although the COS removal capability of a Purisol wash is quite adequate to meet power-plant requirements, it is not sufficient to meet the needs of the copper and nickel catalysts of the low temperature CO shift and methanation units in the hydrogen plant. Apart from Purisol, also other gas purification systems, such as Rectisol and amine based systems should be investigated. Considering the strong reference position of Rectisol especially in SGP syngas cleaning service, Rectisol is an obvious choice for application in gasification in combination with hydrogen manufacture using methanation. Rectisol is, like Purisol, a physical wash and as such shares many of Purisol's above mentioned characteristics. It is slightly less selective but for this application has the advantage of removing COS to levels of under 100 ppb in the clean gas and has a long track record of treating SGP gas upstream of copper catalysts for methanol synthesis. In flow schemes where the hydrogen is a small part of overall production, or where it is produced by PSA, the optimum would tend back to Purisol. Where methanol is a co-product, Rectisol would be favoured again.

3.1.5 Overall Flow Sheet

The result of tailoring available process options for the requirements of Pernis can be seen in the block flow diagram (Figure 2).

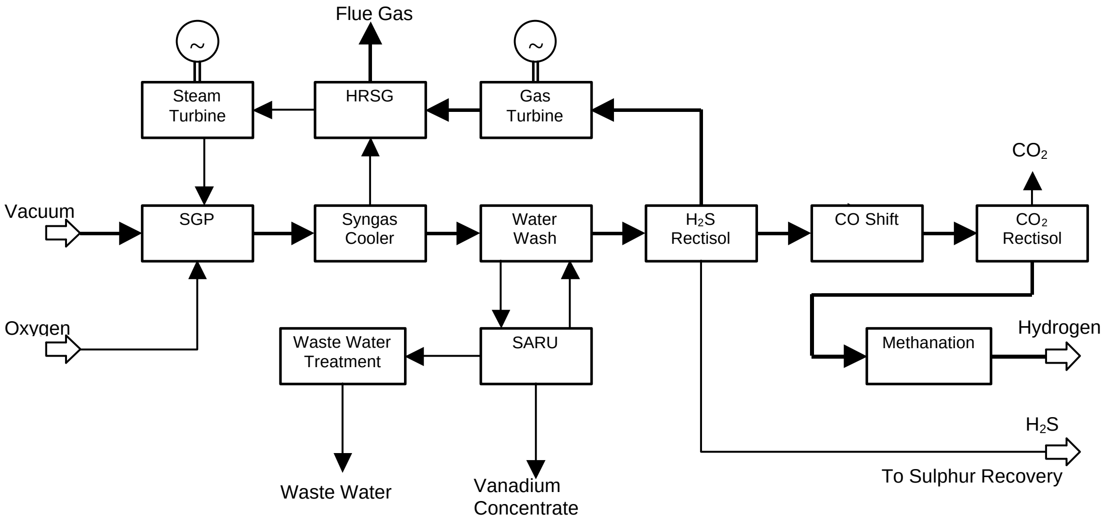

Figure 2: **SGP-based Hydrogen Plant (SGHP)**

The feedstock is gasified in the SGP reactor with oxygen to produce raw synthesis gas at a temperature of about 1200 - 1500 °C and a pressure of about 50 - 70 bar. This gas is a mixture of hydrogen and carbon monoxide which, however, also contains CO_2, H_2S and COS together with some free carbon and the ash from the feedstock.

The hot gas is cooled in the synthesis gas cooler by generating high pressure steam. Particulates are removed from the gas using a water wash prior to desulphurization.

Desulphurization is effected using the Rectisol process. At the SGP/Rectisol interface a scheme has been developed to prevent flaring of sulphur at start-up. Fuel gas is drawn off at this point for the power plant. The remaining gas is then shifted to convert the CO to CO_2 and hydrogen. The gas is methanated after CO_2 removal, giving a 98% H_2 product with under 10 ppm carbon oxides.

3.1.6 Side stream Units

The wash water from the particulate removal is treated in the Soot Ash Removal Unit. Carbon and ash are separated from the water by filtration. The filter cake is worked up by controlled oxidation to a saleable vanadium concentrate. The bulk of the water is recycled to the water wash.

The desulphurization solvent regeneration system operates selectively and without an additional concentration step produces a gas of sufficiently high H_2S content to allow it to by processed to elemental sulphur in the sulphur recovery unit. In many instances it is favourable to utilize the Lurgi oxygen Claus process at this location, either to debottleneck existing units or for new plants.

4 The SHELL Gasification Process ("SGP")

4.1.1 Gasification

The non-catalytic partial oxidation of hydrocarbons by the SHELL Gasification Process (Figure 3) takes place in a refractory-lined reactor, which is fitted with a specially designed burner. The oxidant is preheated and mixed with steam prior to being fed to the burner. The burner and reactor geometry are so designed that this mixture of oxidant and steam is intimately mixed with the preheated feedstock.

4.1.2 Waste Heat Recovery

The product of the partial oxidation reaction is a raw synthesis gas at a temperature of about 1200 - 1500°C which contains particles of residual carbon and ash. The recovery of the sensible heat in this gas is an integral feature of the SGP process.

Primary heat recovery takes place in a waste heat exchanger generating high pressure saturated steam in which the reactor effluent is cooled to about 340°C. The waste heat exchanger is of a special design developed specifically for these operating conditions. Part of the steam thus generated is used for feedstock and oxidant preheating; the remainder is superheated for use in CO Shift and in steam turbine drives. Steam conditions are chosen to be optimised with the steam turbine part of the combined cycle.

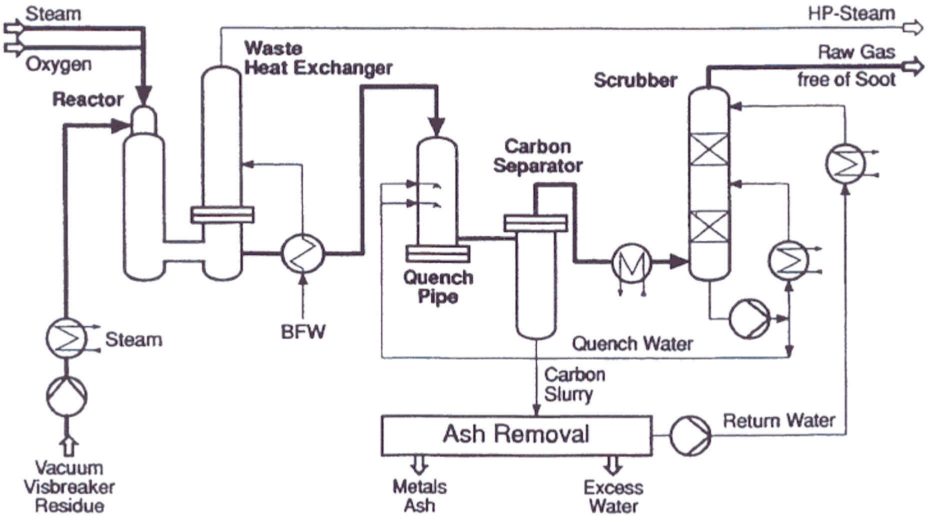

Figure 3: **Residual oil-based SGP Unit**

4.1.3 Carbon Removal

The partial oxidation reactor outlet gas contains a small amount of free carbon. The carbon particles are removed from the gas together with the ash in a two-stage water wash. The carbon formed in the partial oxidation reactor is removed from the system as a carbon slurry together with the ash and the process condensate. This slurry is subsequently processed in the ash removal unit described below. The product syngas leaves the scrubber with a temperature of about 40°C and is essentially free of carbon. It is then suitable for treatment with any commercial desulphurization solvent.

4.2 Ash Removal Unit

Handling the carbon slurry is an important aspect of partial oxidation processes. The trend to using heavier feedstocks with a higher ash content has led to a re-evaluation of traditional extraction methods, in particular the possibilities of recovering the vanadium for metallurgical use.

Figure 4 illustrates the principles of the Soot Ash Removal Unit. The carbon slurry from the SGP unit is flashed to atmospheric pressure in the slurry tank. The slurry is then filtered on an automatic filter to recover a filter cake with about 80% residual moisture and a clear water filtrate. The filter cake is subjected to a controlled oxidation process in a multiple hearth furnace. This type of furnace, which is well established in many industries and specifically in the vanadium industry, allows the combustion of the carbon to take place under conditions where the vanadium oxides neither melt nor corrode. This is not an easy task if one thinks about the problems of burning a high vanadium fuel oil in a conventional boiler. The product is a vanadium concentrate, which contains about 75% V_2O_5.

Compared to the old naphtha extraction-based recycle system, the new once-through process consists of only two processing steps, which are not integrated with the gasification section of the unit.

An additional benefit of this development is increased feedstock flexibility, both for the SGP itself and for the refinery as a whole. The carbon recycle currently practiced has the feature of also recycling some of the ash, so that the charge pump, burner and reactor system see a higher content of ash than that present in the fresh feed. The elimination of the recycle thus allows one to use feeds with considerably higher ash contents than previously. Current experience of over 1000 wppm vanadium at the reactor inlet would be directly applicable to residues of this quality. This is certainly an important feature when reviewing the possibility of introducing heavier (and cheaper) crudes into the refinery.

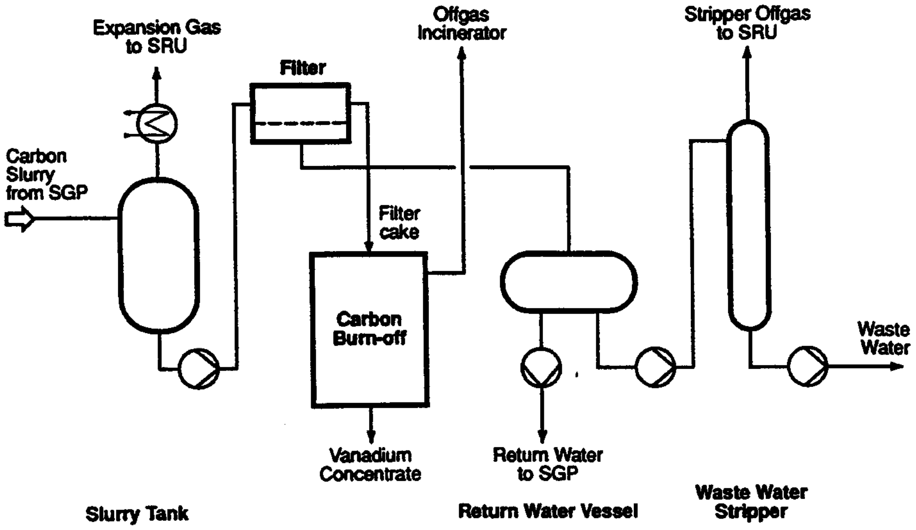

Figure 4: Soot Ash Removal Unit

4.3 RECTISOL Desulphurization and CO_2 Removal

Returning to the Block Flow Diagram, we see the desulphurization and CO_2 removal stages using the selective Rectisol process.

Rectisol (Figure 5) is a physical washing system which uses cold methanol as its solvent. Both H_2S and COS are washed out of the incoming raw gas with the -30°C cold methanol to a residual total sulphur content of less than 100 ppb, a purity which is sufficient for use with the copper-based methanol catalyst without further processing.

The desulphurized gas used for hydrogen production is then shifted outside the Rectisol unit. Carbon dioxide is then removed from the shifted gas in the CO_2 Absorber. This column is divided into two sections, a bulk CO_2 removal section using flash regenerated methanol and a fine CO_2 removal section in which hot regenerated methanol is used. The CO_2 removal operates at lower temperatures than the desulphurized section, at about -60°C. The permissible CO_2 slip is dependent on the application. For hydrogen production based on methanation, typically 100 ppm would be appropriate.

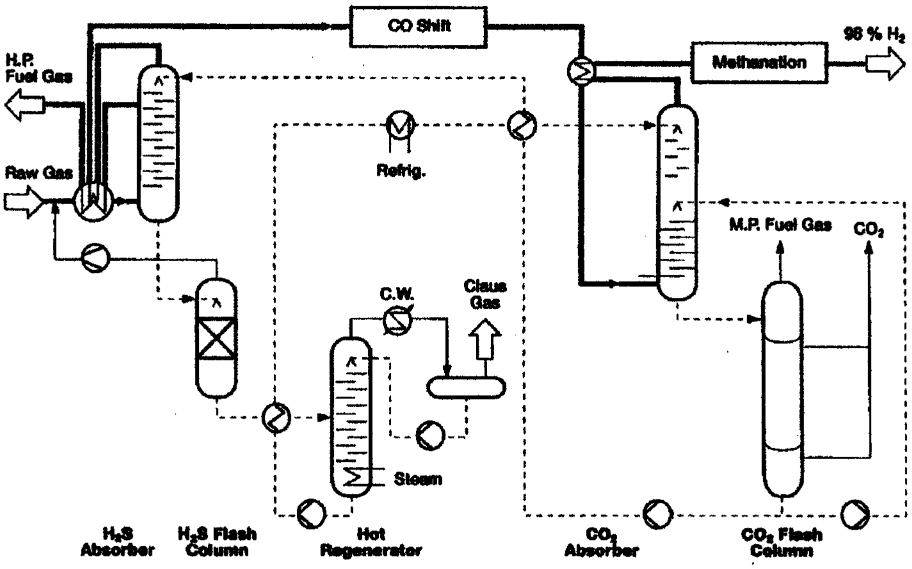

Figure 5: Selective Resctisol procees in SGHP

5 Environmental Aspects

This paper has concentrated on the SGHP part of an overall refinery modernization project. Evaluation of the environmental impact can, however, only be performed in the context of the overall project.

The data in tables 2 & 3 is taken from the article by Ladeur and Bijwaard which describes the SHELL Pernis project. The refinery mass balance of table 2 shows a decisive shift to high sulphur crude, increasing the total sulphur intake from 280,000 t/y to 410,000 t/y.

	Before 1993 [MMt/y]	**After 1997 [MMt/y]**
Intake		
High-sulphur crude	11.3	15.0
Low-sulphur crude	4.5	2.8
Other feedstocks	2.1	0.1
Total Intake	***17.9***	***17.9***
Output		
White product make	12.8	14.0
Fuel oil make	3.5	2.1
Sulphur	0.11	0.30
Total Output	***16.4***	***16.4***

Table 2: Refinery Mass Balance

Nonetheless, the refinery SO_2 emissions are reduced from 35,000 t/y to 24,000 t/y. Sulphur in products is reduced similarly from 150,000 t/y to 100,000 t/y.

Similar reductions can be seen for NO_x and particulate emissions. CO_2 emissions from the refinery increase but because of the lighter product slate, global CO_2 emissions are hardly affected.

		Before 1993	**After 1997**
Refinery emissions			
SO_2	[Mt/y]	35	24
NO_x	[Mt/y]	12	7
Particulates	[Mt/y]	4.0	1.9
CO2	[MMt/y]	5.0	6.1
Global emissions – refinery and products			
SO_2	[Mt/y]	348	206
CO_2	[MMt/y]	56.6	56.8

Table 3: Refinery and Global Emissions

6 Conclusion

Both SGP and Rectisol technologies can play a key role in the implementation of refinery modernization projects like that in Pernis. Their selection and incorporation into the overall scheme must be the result of careful evaluation tailored to the needs of the individual refinery.

With the execution of its project, SHELL has succeeded in

- increasing the high sulphur crude from 63% to 84% of the total intake
- increasing the white product make from 78% to 85% of total output
- reducing fuel oil make by 40%
- reducing by one-third the sulphur in refinery products
- reducing by one-third the refinery sulphur emissions.

These are important steps in the direction of the zero-residue refinery.

References

[1.] **Ladeur, P. and Bijwaard, H.,** "Shell plans $ 2.2-billion renovation of Dutch refinery", Oil & Gas Journal· April 26, 1993· pp 64-67

[2.] **Heurich, H. and Higman, C.,** "Partial Oxidation in the Refinery Hydrogen Management Scheme", AIChE 1993 Spring Meeting, Houston

[3.] **Anon,** "SHELL PERNIS Klaar voor de volgende eeuw", Shell Nederland Raffinaderij B.V., January 1993

[4.] **Higman, C. and Grünfelder, G.,** "Clean Power Generation from Heavy Residues", Inst. Mech. Eng., November 1990