Partial Oxidation in the Refinery Hydrogen Management Scheme

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1 Introduction

Both in the United States and in Europe refiners are being forced to review their operations in the light of increasingly severe environmental legislation. Details in these two parts of the world are different, but the focus of this attention in both areas is ultimately concentrated on hydrogen management and bottom-of-the-barrel usage. The Clean Air Act (CAA) in the United States will restrict the benzene levels in motor gasoline, which will lead to a lowering of gasoline reforming severity and thus a diminution of by-product hydrogen, while the increased level of oxygenates in reformulated gasoline makes the consequent lowering of octane number in the reformer product acceptable.

In western Europe the sulphur emission targets for both refinery products and refinery operations are the driving force for change, although benzene reduction may also become a feature in the medium term. This will bring the need for increased quantities of hydrogen for hydrodesulphurization and hydrocracking purposes. Bottom-of-the-barrel disposal by blending visbreaker residue or asphalt into the heavy fuel oil pool will become increasingly unacceptable - even for bunkers. The expectation of having to process increasingly heavier crudes with high concentrations of sulphur and heavy metals in the future only serves to reinforce these trends.

These tendencies are all pushing in the direction of implementing partial oxidation of heavy residues as an integral building block for hydrogen production into the refining scheme. The paper describes the philosophy and execution of such a scheme being implemented in a 10 million t/y grass roots refinery in Europe currently in the engineering phase and which is planned to go on stream in 1996. The concepts described are equally applicable to the restructuring plan for an existing refinery.

2 SGP in the Refinery Flowsheet

There is a long-standing discussion as to whether one should take the hydrogen-addition or the carbon-rejection route to bottom-of-the-barrel treatment. The approach suggested in this paper recognizes that this is a largely academic debate and proposes combining both techniques to achieve an optimum economic and environmental effect.

2.1 The Refinery Flow Sheet

Before entering into a detailed description of the partial oxidation and gas treating technology, however, it is necessary to review how the partial oxidation process fits into the whole refinery picture. What is its location in the overall refinery flowsheet? What products can it produce and how do they relate to the market? What feedstocks can it handle and what are the environmental demands placed on it? Figure 1 shows the refinery configuration which includes a vacuum distillation unit, a solvent deasphalter and a SHELL Gasification Process ('SGP') partial oxidation unit processing the asphalt.

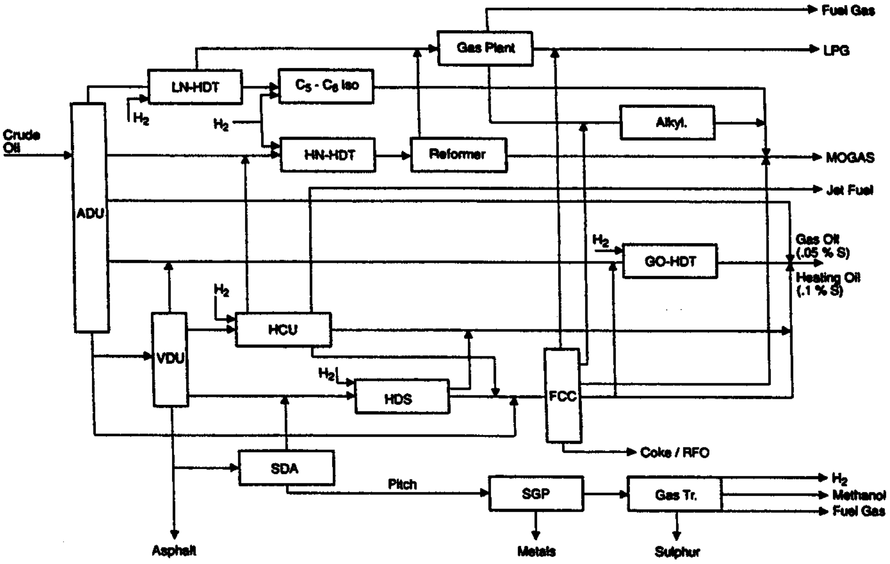

Figure 1: SGP in the Refinery Environment

The refinery configuration is aimed in the first instance at maximizing white products and eliminating any heavy fuel oil export. On the basis of the planned crude slate the total vacuum residue will be about 16% of crude intake. A small proportion of this will exported as street asphalt and the rest is fed to a solvent deasphalter. The SDA unit is capable of recovering up to 50% of the vacuum residue as DAO which after desulphurization is suitable as FCC feed. The resulting asphalt, about 6.5% of intake, is then gasified in the SGP unit.

High Purity (>99.9% H_2)	**Producers [t/d]**	**Consumers [t/d]**
SGP	140	
Hydrcracker		100
VGO/DAO/HDS		40
Total High purity	**140**	**140**
Standard Purity (approx 90% H_2)		
Catalytic reformer	140	
Gasoil HDT		100
Naphtha HDT		20
Isomerization		15
Other		5
Total standard Purity	**140**	**140**

Figure 2: Hydrogen balance

This type of processing produces an asphalt which is high in pollutants, such as sulphur and heavy metals. It also has a high viscosity. And this is where gasification comes in. By gasifying the residue instead of putting it into the fuel oil pool one can extract both major pollutants separately and in an economically usable form. The products of gasification and subsequent gas treatment are methanol, hydrogen and a clean fuel gas.

2.2 Hydrogen Balance

The product slate from the refinery is geared to meeting current or planned European environmental restrictions on sulphur emissions, i.e. 0.05% S in diesel oil and 0.10% S in heating oil, which are due for implementation in 1996 and 1999 respectively. This degree of desulphurization, together with the high degree of bottom-of-the-barrel recovery using both hydrocracker and the SDA/FCC combination requires a large amount of hydrogen - in fact the total refinery hydrogen requirement is nearly 1% by weight of total crude input. The major producers and consumers are listed in Figure 2. The SGP has a larger raw gas production capacity than required by the 140 t/d hydrogen demand as shown. The gas treatment section is in fact designed to allow the pure hydrogen capacity to run up to 150 t/d at the cost of a drop in methanol production. This flexibility allows for a full supply of hydrogen to the heavy end of the refinery (Hydrocracker and HDS) even if later heavier crudes than at present envisaged are processed. Equally a drop in the available asphalt for gasification caused by e.g. a lighter crude can be taken up in the methanol production rate without affecting hydrogen production.

2.3 Feedstocks

Figure 3 shows typical specifications of feedstocks from cracking or deasphalting processes. Important features to notice are the high sulphur content, the high metals content and the high viscosities.

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

Figure 3: Typical SGP Feedstocks

2.4 Environmental Tasks

The resulting four key environmental tasks are:

- reducing sulphur emissions
- reducing CO_2 emissions
- removing heavy metals
- reducing NO_x emissions

Our objective is therefore to accomplish these tasks using a maximum of proven technology to produce a marketable product slate.

3 PROCESS DESCRIPTIONS

3.1 Block Flow Diagrams

A review of the available pitch quantities from the SDA unit in comparison with the net hydrogen demand of the refinery shows that under all circumstances co-manufacture of some other product from the syngas generated is required. Although examples exist where ammonia is the co-product, in today's refinery environment methanol and electric power are the two leading candidates, at least as far as volume products are concerned. In our example refinery the main co-product is methanol. Provision is however made also for the production of Carbon Monoxide should this be required at a later date.

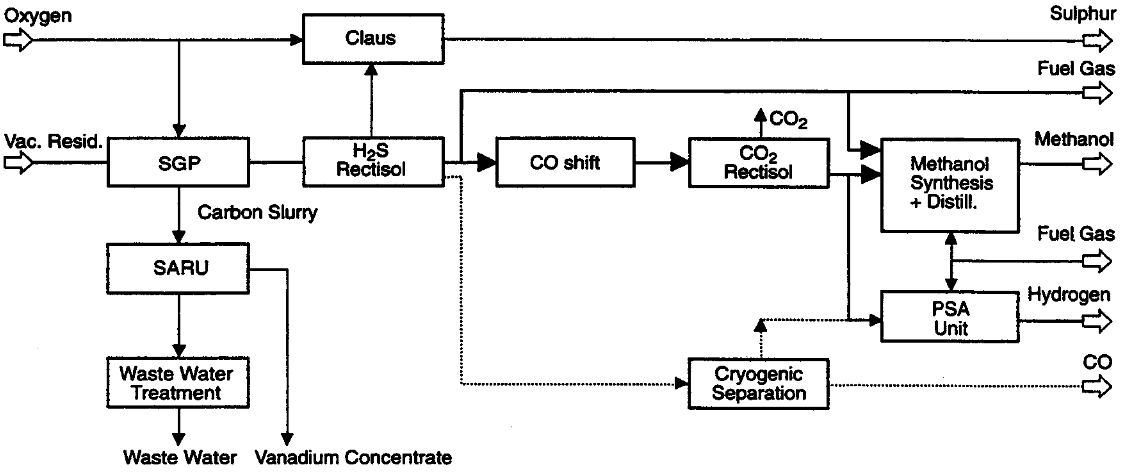

Figure 4: **SGP-based Hydrogen and Methanol Plant**

3.1.1 Hydrogen

When setting up a flow scheme for hydrogen production, the first step must be to define the quality of hydrogen required. Many 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 80% instead of 98%) and the production of a relatively large quantity of low pressure, low BTU fuel gas. It is important in this context to review the hydrogen purity specification carefully with the process licensor of the hydroconversion units, 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. The result of optimization work for this refinery was that the PSA route has been selected.

The block diagram in Figure 4 provides an overview of the total process. The feedstock is gasified in the SGP reactor with oxygen to produce raw synthesis gas at a temperature of about 1300 °C and a pressure of typically about 60 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 in which cold methanol is used as the solvent. The gas is then shifted to convert the CO to CO_2 and hydrogen. A feature of the flow scheme which may be unfamiliar to those used to a steam reformer based hydrogen plant is the inclusion of a CO_2 removal step before the PSA unit. Of course this is not necessary in terms of achieving specification hydrogen. The shift gas however contains about 34% CO_2 which both inflates the cost of the PSA as well as reducing its efficiency. The key issue is however the tail gas quality, which without a CO_2 removal unit would have a heating value of 160 MJ/kmol. Since this is the determining factor it is clear that it is not necessary to remove all the CO_2 by any means and a slip-stream unit for partial CO_2 removal is quite adequate.

3.1.2 Methanol

A side-stream of gas is bypassed around the shift unit to achieve the correct H_2 /CO ratio for the methanol synthesis process before CO_2 removal in a separate absorber, also using Rectisol. The methanol synthesis itself operates at about 80 bar using the LURGI Low Pressure Methanol Process followed by a distillation step to achieve a product quality specification.

3.1.3 Carbon Monoxide

The provision for carbon monoxide production is shown dotted. Carbon dioxide is removed to a deeper level at this point than for hydrogen or methanol before the gas enters the cold box of the cryogenic unit. This produces an on spec CO product for acetic acid production and a > 97% hydrogen stream at about 22 bar. Depending on the overall hydrogen scheme this may be fed through the PSA for final cleanup or used in the refinery without further processing.

3.1.4 Sidestream Units

The wash water from the particulate removal is treated in the Ash Removal Unit. Carbon and ash are separated from the water by filtration. The filter cake is subjected to controlled oxidation in a multiple hearth furnace in which the residual carbon is burnt off leaving a salable 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 be processed in a LURGI Oxygen Claus Technology unit which converts the hydrogen sulphide into elemental sulphur.

3.2 The SHELL Gasification Process ("SGP")

3.2.1 Gasification

The non-catalytic partial oxidation of hydrocarbons by the SHELL Gasification Process (Figure 5) 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.

3.2.2 Waste Heat Recovery

The product of the partial oxidation reaction is a raw synthesis gas at a temperature of about 1300°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 (100 bar) 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 and used in about 135 installations world-wide. 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.

Secondary heat recovery takes place in a boiler feed water economizer immediately downstream of the waste heat exchanger.

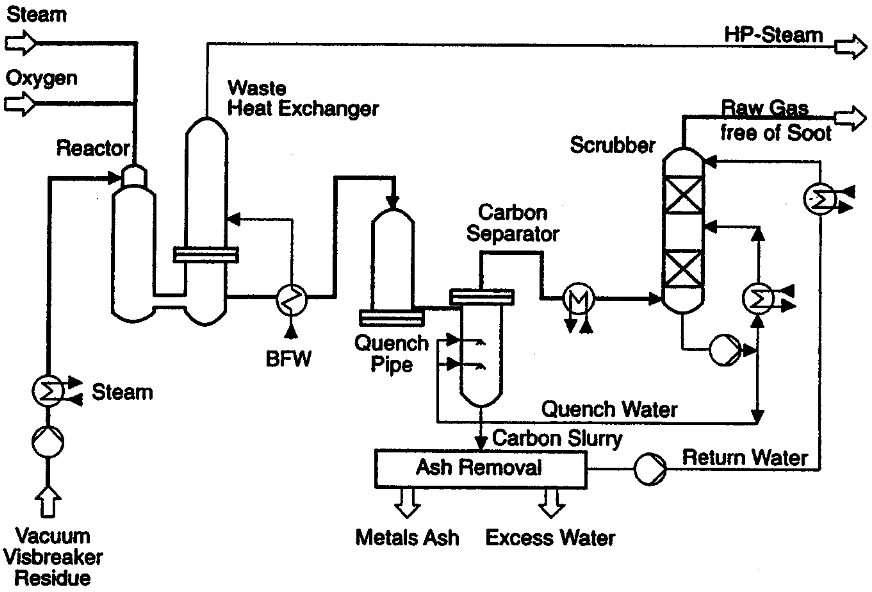

Figure 5: Residual Oil-based SGP unit

3.2.3 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.

Some 140-150 units have been installed world-wide with a processing capacity of some 7 million t/y of residue. One typical reference plant processes about 240,000 t/y of residues of varying quality which are bought on the open market, for the production of ammonia. Another which was started up in 1972 produces a a mixed product slate of ammonia, methanol and hydrogen and is fed with about 350,000 t/y residue directly out of a visbreaker.

3.2.4 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 reevaluation of traditional extraction methods, in particular the possibilities of recovering the vanadium for metallurgical use.

Looking at the pitch quality we see that at the feed rate of 100 t/h an annual total of some 320 tons of vanadium enters the plant. This amount of heavy metal waste represents a substantial environmental problem and high cost if one has to dump it. On the other hand if one can recover it in a form which is useable in the metallurgical industry, both the environmental issue and physical disposal can be simultaneously be resolved. And even if the vanadium price is currently not particularly attractive, this can now be performed without extra cost using a recently developed process route.

Figure 6 illustrates the principles of the SHELL 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. The process is autothermal, the heat of combustion of the carbon being sufficient to evaporate the moisture content of the filter cake.

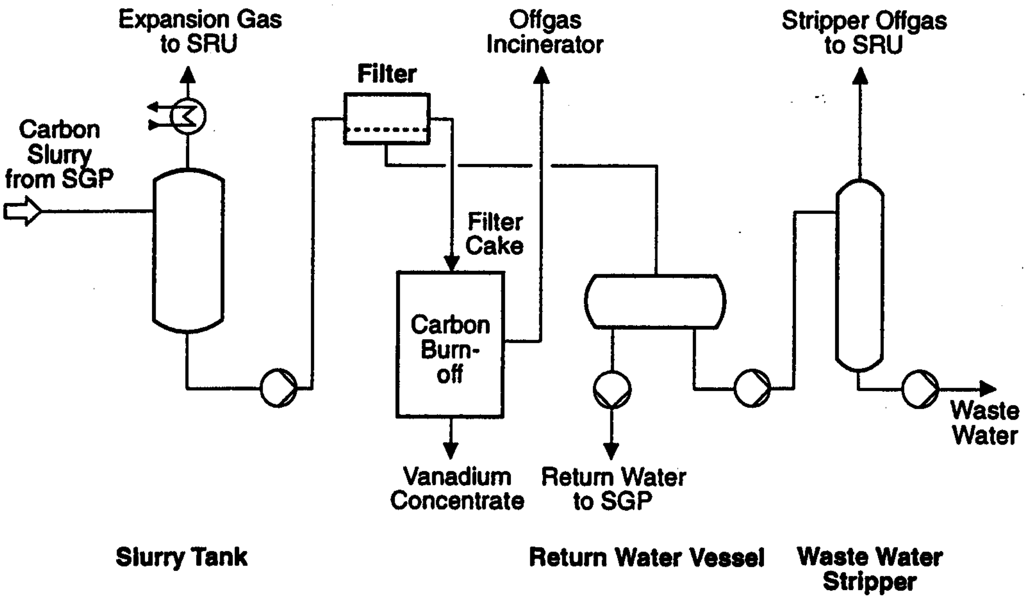

Figure 6: Shell Ash Removal Unit

The process is fundamentally simple, a fact which is reflected in a markedly lower capital cost than that of extraction processes. Surprisingly enough the operating costs are also lower since the energy saving achieved by eliminating the necessity for naphtha recovery more than compensates the losses incurred by not recycling the carbon to the SGP reactor.

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.

The bulk of the filtrate is recycled as wash water to the SGP unit. However, the overall system generates a net water surplus which must be further treated before final discharge. The first step is a sour water stripper in which dissolved gases, such as H_2S, CO_2 and ammonia are removed. The stripped gases are incinerated in a special burner in the Claus unit and therefore kept entirely within the system.

Final water clean-up takes place in a flocculation-sedimentation system for trace metal (ash) removal and a biological waste water treatment unit.

3.3 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 7) 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.

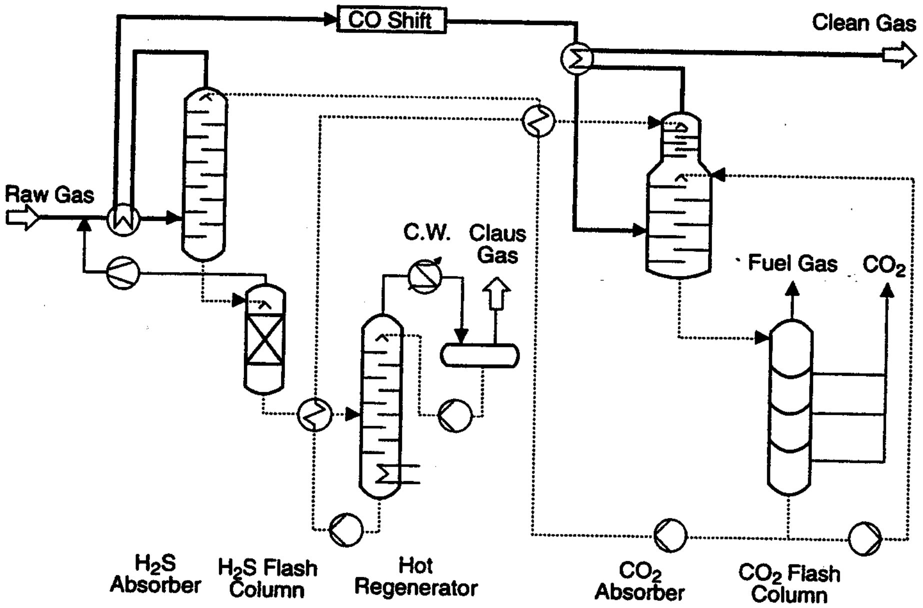

Figure 7: Rectisol Acid Gas Removal Unit

If a carbon monoxide production unit is incorporated into the scheme, then hot regenerated methanol is used to remove residual CO_2 from the feed gas to the cryogenic separation unit before being utilized in the CO_2 wash.

The desulphurized gas used for hydrogen production and for adjusting the stoichiometry of the methanol synthesis gas 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 desulphurization section, typically at about -60°C. The permissible CO_2 slip is dependent on the application. For methanol synthesis gas 1% residual CO_2 is quite adequate. For hydrogen production based on methanation, typically 100 ppm would be appropriate. This is of course the carbon rejection part of the scheme, even if it takes place in the form of CO_2 rather than of coke. However, one of the important features achieved by using a physical rather than a chemical solvent is the fact that over 20% of the CO_2 is available at about 5 bar which allows further processing for e.g. food use with reduced compression duty.

3.4 CO Shift Conversion

Now we come to the hydrogen addition step, in which the carbon monoxide produced in the Gasification unit is converted with steam to produce hydrogen and carbon dioxide according to the equation

$$CO + H_2O \implies H_2 + CO_2.$$

The flow sheet of the CO Shift Conversion Unit (Figure 8) shows a saturator-cooler system which uses the heat of reaction of the CO shift reaction to generate two-thirds of the thermodynamic steam requirement of the reaction. Only the stoichiometric steam requirement is drawn from the header. This represents approximately 32% of the net steam produced in the SGP unit, the balance being available for steam turbine drives. A two-stage reactor system using conventional HT-Shift catalyst is used to achieve a CO slip of about 3.2 %.

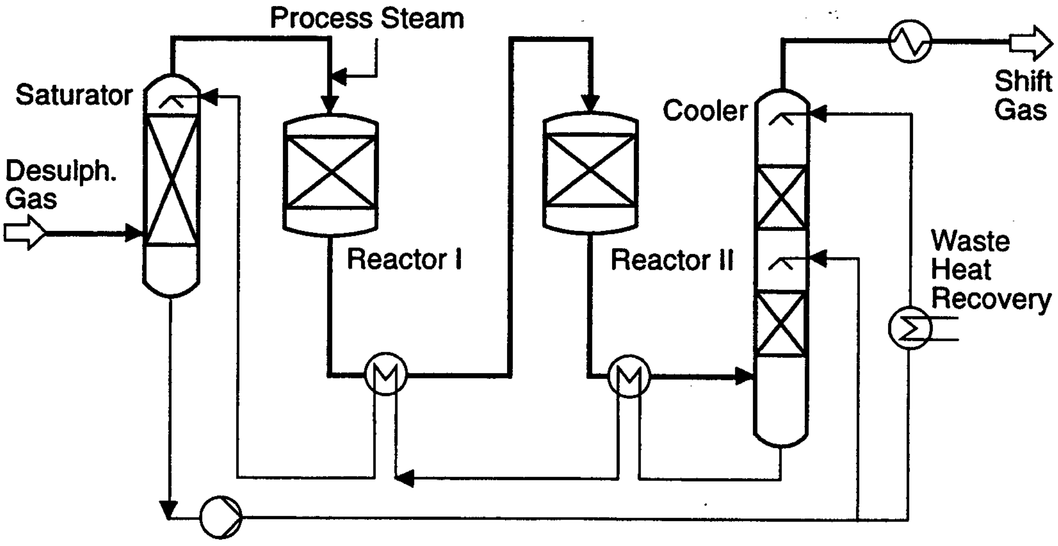

Figure 8: CO Shift Unit

3.5 LURGI Low Pressure Methanol Process

3.5.1 Methanol Synthesis

Correct adjustment of the bypass around the CO Shift unit will allow the production of a synthesis gas with an optimum value of just over 2 for the stoichiometric ratio $(H_2\text{-}CO_2)/(CO+CO_2)$. The selection of the exact pressure to run the methanol synthesis loop will depend on an OPEX/CAPEX optimization. For medium size units of for instance 600 t/d the loop would operate at about 50 bar, i.e. without any intermediate syngas compression. For a large unit of say 2000 t/d, the optimum pressure is some-what higher. The principles are shown on Figure 9.

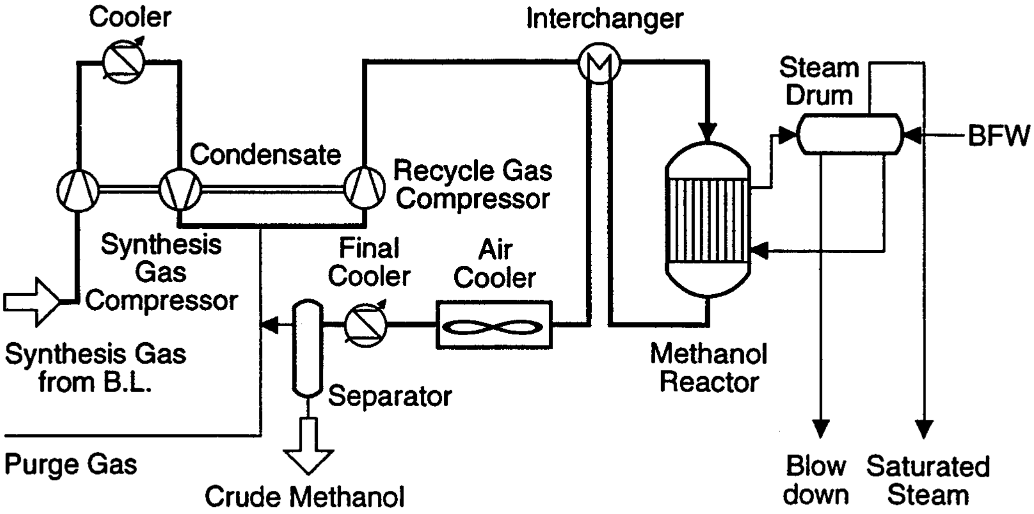

Figure 9: Methanol Synthesis Unit

The clean gas from the CO_2 removal unit is compressed to the methanol loop pressure and then preheated in the Feed-Effluent-Exchanger. The carbon monoxide and hydrogen are converted to methanol in a tubular reactor in which the tubes are filled with catalyst and cooled by the boiling water surrounding them. The steam pressure of about 40 bar maintains the desired reaction temperature of 250°C. The unconverted gas together with the methanol leaves the reactor and is cooled and the methanol condensed. The crude methanol is separated out in a separator and led to the distillation section. Inerts (mainly $CH_4$and N_2) are purged from the loop before the remaining gas is fed back to the circulator. The purge gas, which in the case of a partial oxidation based methanol plant is relatively small, contains also some H_2 and CO and is used as a sulphur-free fuel gas within the partial oxidation complex. The steam generated in the reactor is sufficient to run the compressor driver which is a back-pressure turbine. The exhaust steam from the turbine in turn provides the heat for the distillation section.

3.6 LURGI Oxygen Claus Technology

Since we have introduced oxygen as a medium into the complex it is well worth looking at the benefits of operating the Claus unit on oxygen. The Claus unit uses a

LURGI developed multipurpose Claus oxygen burner which allows the use of air, oxygen-enriched air or pure oxygen. This has the advantage of reducing capital expenditure on a new plant since the gas volumes are substantially reduced. It is also capable of handling lean acid gas with H_2S contents as low as 10%, thus reducing the selectivity requirement on the acid gas removal unit. In addition it is designed to cope with NH_3 containing streams from the sour water stripper and the carbon slurry flash.

4 PLANT FLEXIBILITY

The production and consumption data in Figure 10 show the flexibility of the plant. The typical nominal normal operating case without CO production is 5 t/h pure H_2 and 2090 t/d methanol. The actual design allows however for considerable flexibility depending on the demands put on the plant by the refinery as described earlier.

Feed	Products			
Asphalt [t/h]	Hydrogen [t/h]	Methanol [t/d]	CO [Nm^3/h]	Fuel Gas [t/h]
100	5.0	2090		
100	6.5	2050		
100	5.0	1990	20 000	
100	5.0	1200		
80	5.0	1690		

Figure 10: Production and Consumption Figures

5 ALTERNATIVE LINE-UPS

Although the above description is based on one particular refinery scheme, it is certainly of interest to show two alternative line-ups being used on current projects. The first (Figure 11) is the cogeneration of electric power with hydrogen being employed in SHELL's Pernis refinery in Rotterdam, a project now in the detail engineering phase and due for start-up in 1997. Apart from the takeoff of desulphurized syngas to feed existing and new gas turbines one can see the methanation route for hydrogen production. This configuration is part of a major restructuring project in one of Europe's largest refineries.

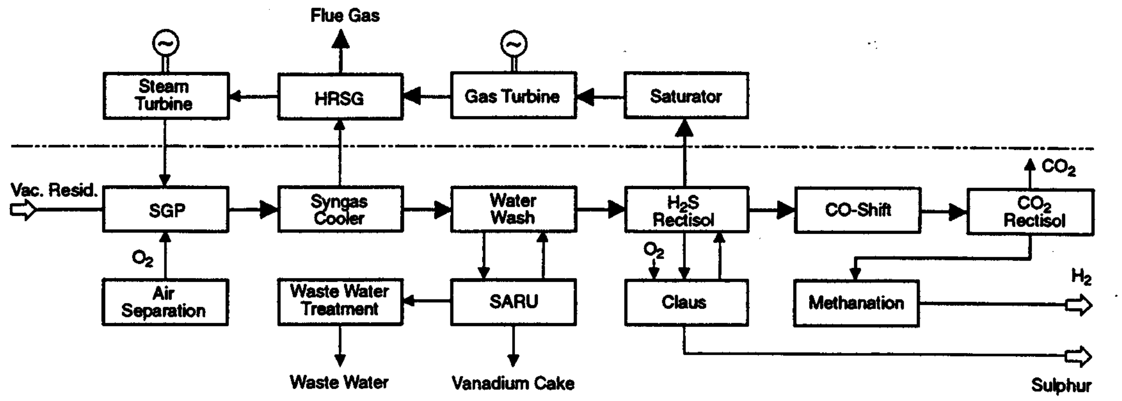

Figure 11: SGP-based IGCC and Hydrogen Plant

It is interesting to note that for studies we are preparing for a unit of similar size in a grass roots refinery in the far east, PSA without prior CO_2 removal is the purification system of choice (Figure 12).

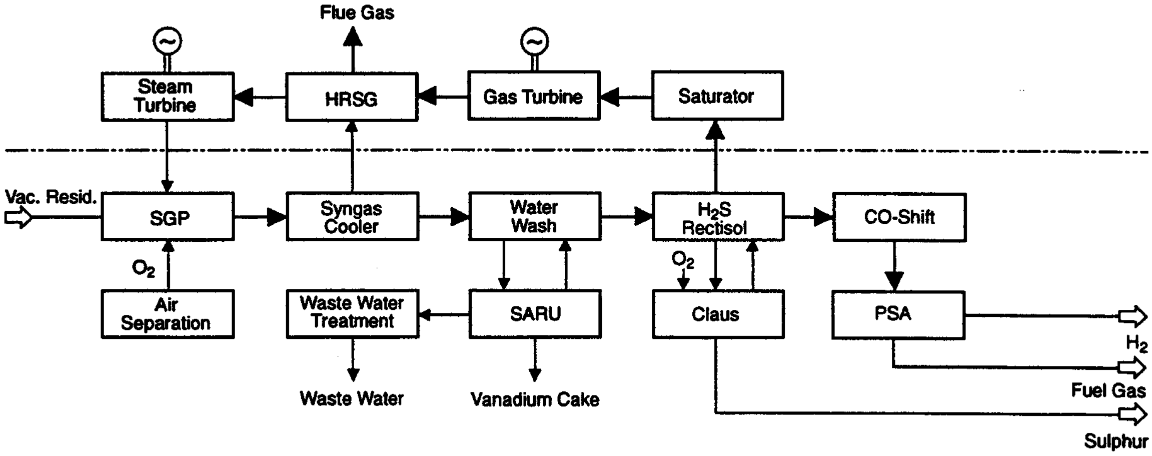

Figure 12: SGP-based IGCC and Hydrogen Plant with PSA

6 ENVIRONMENTAL ASPECTS

Earlier we set ourselves certain key environmental tasks. The environmental data in Figure 13 provide the basis for examining how well these challenges are met. They are based on an IGCC power application so as to be able to highlight the NO_x capability in such cases, even if this aspect is less relevant for the hydrogen/methanol combination.

Pollutant		**SGP-IGCC**	**Emission Limits**	**Regulation**
Flue Gas				
SO_x	[mg SO2/m^3]	20 - 40	400	13. BImSchV
Sulphur recovery	[%]	99.6 - 99.8	85	13. BImSchV
NO_x	[mg NO2/m^3]	60 - 150	150	Umweltminister Konferenz 5.4.84
Particulates	[mg/m^3]	<0.5	50	13. BImSchV
Waste Water				
Vanadium	[mg/l]	<2	3 2	31. Abwasser VwV City of Hamburg
Nickel	[mg/l]	<1	3	City of Hamburg
BOD_5	[mg/l]	<20	25	45. AbwasserVwV

Figure 13: SGP-based IGCC: Environmental Characteristics

6.1.1 Sulphur

The partial oxidation process takes one of the most sulphur rich streams of the refinery and, in combination with Rectisol and oxygen Claus technology, is able to achieve a sulphur yield of over 99.5% on the liquid feed stream as well as producing hydrogen required for desulphurization of other refinery streams. It is also able to produce a clean fuel gas to substitute for fuel oil in process heaters in the refinery.

6.1.2 Heavy Metals

The newly developed SHELL Ash Removal Unit allows the metallic ash present in the feed to be processed economically to a vanadium rich concentrate suitable for use in the metallurgical industry. Combined with suitable waste water treatment technology it can continue to meet environmental legislative targets even with the higher metal contents to be expected in tomorrows crudes.

6.1.3 Carbon Dioxide

The introduction of methanol as co-product for hydrogen production fixes a substantial portion of the carbon in the feed in a product which is required for reformulated gasoline, be it directly or in the form of MTBE. Using the partial oxidation unit in conjunction with a combined cycle power plant, efficiencies of about 44% can be achieved, a significant improvement in CO_2 emissions per MW produced when compared with conventional combustion technology. Some of the directly rejected carbon dioxide is available under pressure allowing it to be sold as merchant CO_2.

7 CONCLUSION

As can be seen gasification of heavy residues has an important part to play in the development of deep conversion refinery schemes. The flexibility of the product slate from the raw syngas allows adaptation of the refinery configuration to accommodate the stringent environmental demands now being placed on US and European refineries. The concept of a "zero residue refinery" is now more feasible with heavy oil gasification of the bottom-of-the-barrel.

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