Perspectives and Experience with Partial Oxidation of Heavy Residues

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1 Introduction (or Why?)

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-suphur 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. Realisation that coke disposal is becoming increasingly difficult has led to wider application of residue gasification (or partial oxidation 'POX'). Three existing refineries in Germany already employ the SHELL Gasification Process (SGP) in on-plot plants for residue utilisation. A fourth stand-alone gasification plant takes up residue from refineries in the Hamburg area, bringing the material by heated barges some 100 km down the River Elbe. A total of about 150 gasifiers have been built world-wide using this process alone. A further nine are currently under construction including a major revamp at SHELL's own Pernis Refinery near Rotterdam.

This paper reviews some of the experience gained in the existing plants and influences on current and future design.

2 Feedstocks and Products (or Where?)

Before entering into a detailed description of the technology, however, it is necessary to review how the SGP fits into the whole refinery picture. What is its location in the overall refinery flowsheet? What feedstocks can it handle? What are the environmental demands placed on it? What products can it produce and how do they relate to the market?

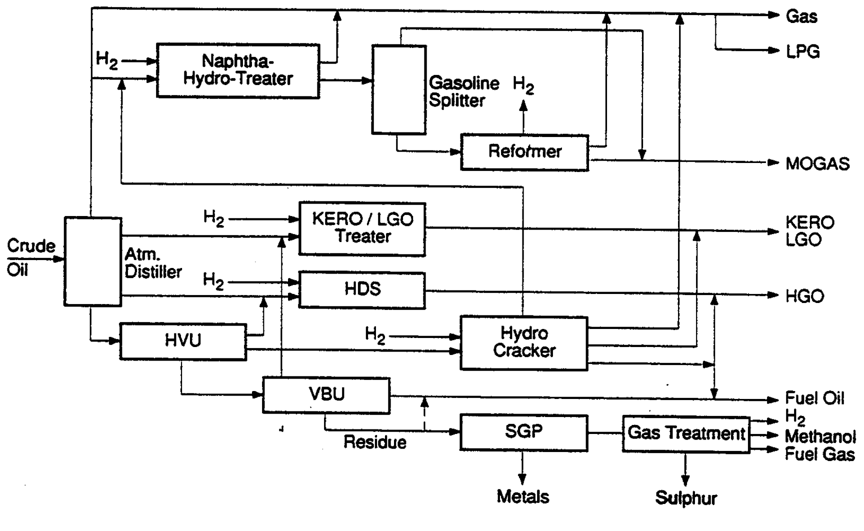

Figure 1 SGP in the Refinery Environment

Figure 1 shows a typical refinery configuration which includes a vacuum distillation unit, a visbreaker and an SGP processing the visbreaker residue.

2.1 Feedstocks

Historically the SGP process, which was initially developed in the 1950's, began by gasifying fuel oil and bunker C material. As time went on the feeds became heavier and heavier. Viscosities became higher as did the content of sulphur and heavy metals. By the 1970's vacuum residue had become the standard feed. In today's refinery environment it would be exceptional to have a feed lighter than a visbreaker residue or a butane asphalt, for which typical properties are listed in Table 1 below. Heavier feeds such as pentane asphalt have been run extensively in the SHELL pilot plant facility in Amsterdam, although there are no commercial applications for such a feed at present.

In individual cases considerably higher values than those in the table have been experienced. Other impurities - mostly metals - have also been encountered. A discussion of some of these will be made later in this paper.

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

2.2 Market Applications

Table 2 shows a list of applications for SGP - all of which, with the exception of the utilities are (or in the case of towns gas have been) in commercial operation.

When looking at the market possibilities it is necessary to try to match the sales volumes of the product with the total volumes of residue available. Of those products of immediate use in the refinery, hydrogen is an obvious choice. Advanced processing schemes consume large quantities of hydrogen. Whether the demand will match the quantities of residue available will of course depend on the overall refinery configuration. Methanol, either as a direct fuel additive or as a feedstock for MTBE production can account for some additional residue. Ammonia prices are too low to make it attractive and there is no marketing synergy as might be the case with methanol. The speciality chemicals do not generate sufficient volumes to make any impact on the residue problem, although a sidestream unit on a base plant might offer possibilities for a high margin investment. The market for electrical power as another possibility for absorbing the quantities of residue available is becoming of increasing importance.

Bulk Chemicals
- Ammonia from residual oils
- Methanol from residual oils

Refinery Applications
- Hydrogen from residual oils

Synfuels
- Diesel/Gasolinr from natural gas

Speciality Chemicals
- Oxo-Alcohols (detergents, plasticiser)
- CO for acetic acid
- CO for phosgene, isocyanates, polyurethane, acrylics etc.

Utilities
- Clean fuel gas from residual oils
- Combined cycle power from residual oils

Other
- Reduction gas
- Town gas

Table 2: Market applications for SGP

Looking as an example at the four German plants mentioned earlier, we can see the following spread of products with the accompanying quantities of residue used for the different applications:

Product	[t/d]	Residue [t/d]
Methanol	3420	2620
Ammonia	2650	2030
Hydrogen	210	1056

Comparing this with a product plate determined by other circumstances we see a rather different situation in the SHELL Pernis project, where hydrogen and power are the main products, a considerable shift compared with projects from the 1970' and 1980's.

Product		Residue [t/d]
Hydrogen [t/d]	255	1100
Power [MW]	115	550

3 Process Description (or What?)

3.1 The SHELL Gasification Process ("SGP")

Before going further into details of operational experience it is necessary to run briefly through the flow sheet of a gasification system. The main features are the gasification itself, in which the feedstock is reacted to raw synthesis gas ($CO+H_2$), the synthesis gas cooling and the carbon handling system.

Gasification

The non-catalytic partial oxidation of hydrocarbons by the SHELL Gasification Process (Figure 1) 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.

The burner management system includes a sophisticated safeguarding system as well as a sequence logic block which allows the start-up to be very largely automated.

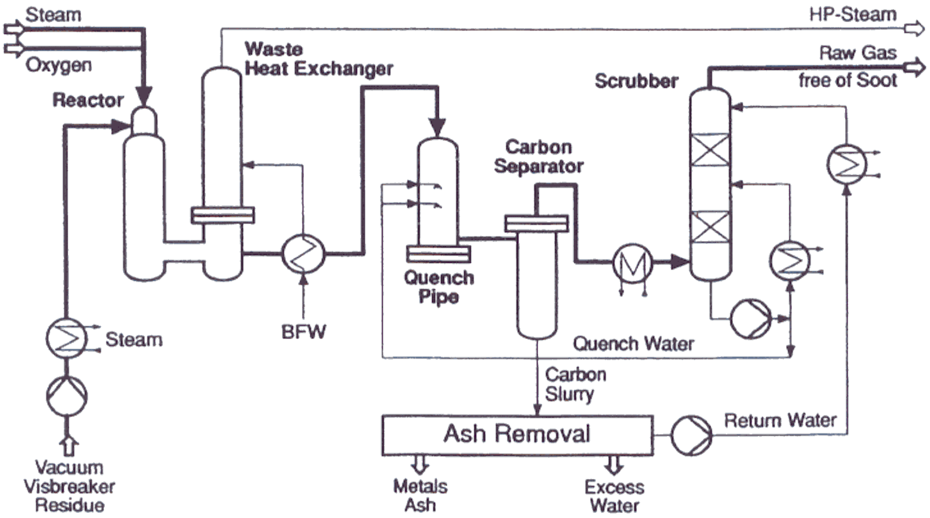

Figure 2: Residual Oil-based SGP Unit

Syngas Cooling

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 steam turbine drives.

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

Carbon Removal

In the partial oxidation of hydrocarbons the product gas contains a certain amount of free carbon. The plant is designed for a free carbon content in the gas (carbon make) equivalent to about 1 wt% of the reactor feedstock. The carbon particles are removed from the gas together with the ash in a two stage water wash. This consists of a quench pipe and carbon separator followed by a packed tower, the carbon scrubber. In the quench pipe about. 95% of the carbon is removed by direct water spray. In the scrubber the gas is washed in countercurrent flow in two packed beds. A circulation system is employed over the lower bed using a circulating pump. The upper bed is washed with return water from the carbon recovery section.

The carbon formed in the partial oxidation reactor is removed from the system with the process condensate as a carbon slurry. This slurry has a carbon content of about. 1% carbon. It is then processed in the carbon recovery unit described below. After carbon removal this water is then recycled as return water to the top of the scrubber. After leaving the scrubber with a temperature of about 40 °C the gas has a residual carbon content of about 1 mg/m3 and is suitable for feeding to the desulphurization unit.

Carbon Recovery Unit

The traditional approach to handling the carbon slurry was to contact it with a hydrocarbon to retain the carbon which could thus be recycled back to the reactor. The early SHELL units used fuel oil as the extraction medium. This allowed atmospheric operation, providing a plant with low investment costs and, at least initially also low operating costs. The economics of this approach deteriorated with heavier feedstocks. The pelletizing oil had to be purchased at a premium to the main feedstock and with higher ash contents 100% carbon recycle became well-nigh impossible as most of the ash was recycled as well.

The logical development of the process was to use naphtha as the extraction medium. Soot is extracted from the water with naphtha as pellets. These naphtha-soot pellets are sieved off from the water and then mixed in with the main feedstock at whatever temperature is required to achieve the desired viscosity. The naphtha is then distilled off from the feed for recycle to the extraction stage leaving the soot behind in the feed. The use of naphtha as an intermediate allowed the use of heavier more viscous feedstocks than pelletizing with fuel oil. Also the improvement in separation of carbon and ash allowed 100% recycle. Nonetheless an ash build-up factor of about 3:1 can be observed under 100% carbon recycle conditions. The plant is costlier than fuel oil pelletizing both in investment and operation.

These facts have led to the review and finally the development of an alternative approach, which will be discussed later.

Waste Water Pretreatment

The run-down water from the sieve contains traces of naphtha and the ash. In the waste water pretreatment section the bulk of the water is recovered for reuse as wash water for carbon removal. First the naphtha is stripped out and returned to the naphtha circuit. Then the ash is separated from the water and demoisturized in a filter press. The filter cake thus produced is a saleable by-product containing 25% - 30% wt of vanadium. This degree of treatment is sufficient for the recycle water.

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. An important feature of the process is the ability to extract the potentially toxic heavy metals (vanadium or nickel) in a saleable form suitable for the metallurgical industry - a beautiful example of turning a disposal problem into a secondary source of raw materials, while at the same time achieving an acceptable waste water quality.

4 Reference Performance (or How long?)

As mentioned earlier the partial oxidation process was developed during the 1950's. Since then some 150 or more SGP units have been installed world-wide with a processing capacity of some 7 million t/y of residue.

Typical reference plants include the following:

- A plant in Germany which was started up in 1972 produces a mixed product slate of ammonia, methanol and hydrogen and is fed with about 350 000 t/y residue directly out of a visbreaker. During the first year of operation the SGP unit achieved a unit reliability of 99.4% of a planned 8000 hr annual running time. A list of plant trips during this time showed the following frequencies:

Cause of trip	**Frequency**
Failure of control valves, motor-operated valves and other valves	13%
Steam failure	2%
Oil pump failure	3%
Oxygen supply failure	12%
High reactor temperature	7%
Electrical failure	8%
Other causes in the gasification unit	5%
Other causes outside the gasification unit	50%

  This plant is still operational and regularly reports annual availabilities in the order of magnitude of 98%.

- Another plant of similar size, built for the same client, but this time not integrated in an existing refinery. This plant purchases feedstock on the open market at the cheapest prices available. Most of the feed has been visbreaker vacuum residue, bitumen or asphalt. This has resulted in the plant having to process much heavier and more difficult material than that originally specified. The comparison between design and practice for the reactor feed (after allowing for the recycle) is shown in Table 3.

  This plant was equipped with a fuel oil pelletizing system, which had been fully adequate for the original design specification. Here one can see the effect of recycle on the actual feed to the reactor in a particularly extreme form. While no detrimental effects could be seen on equipment performance at 1000-2000 mgV/kg, it was these levels of ash which led to the fundamental rethink of the carbon handling process described later.

		1975 design	**1988 operation**
Recycle rate	[%]	85	100
Ash	[wt%]	0.1	1.5
Fe	[mg/kg]		464
Ni	[mg/kg]		1060
V	[mg/kg]		6755
V+Ni+Na	[mg/kg]	400	8400

Table 3: Feed quality including soot recycle

Another interesting point about the experience in this plant is the waste water quality. Most SGP units are located in refineries so that it is generally difficult to separate the final discharge of the waste water from SGP from that of other refinery units. This one, however, was built on a green-field site where such isolation is possible. The strict German waste water standards are maintained.

- Another plant processes about 240 000 t/y of residues of varying quality which are bought on the open market for the production of ammonia. A similar trip analysis for this plant to that shown earlier is of interest.

Cause of trip	**Frequency**
Failure of control valves, motor- operated valves and other valves	5%
Steam and BFW failure	18%
Oil pump failure	5%
Oxygen supply failure	20%
High reactor temperature	0%
Electrical failure	5%
Other causes in the gasification unit	2%
Other causes outside the gasification unit	29%
Leaking flanges	9%
Sheduled	7%

  The considerable reduction of trips attributable to control and motor operated valves within the unit in worthy of note. The main reason for this improvement was considerably tighter specification and testing procedures introduced for the valves in oxygen service, which in the earlier plant had had a tendency to stick. The steam system was however not as robust, since it was not integrated into a large refinery-wide network as the earlier plant had been. The loss of oxygen supply was largely attributable to faulty instrumentation in the compressor area. This was an experience Lurgi made almost simultaneously in another plant using a different, but still oyxgen-based technology. This is an area in which such problems are not inherent to the process but still require much attention to detail to ensure a quality commensurable with the importance that the oxygen supply has for the overall plant.

- A fourth plant is also worthy of mention, a plant processing 800 000 t/y vacuum visbreaker residue for the production of methanol and clean syngas, most of which was treated in existing units to produce hydrogen, either for refinery purposes or for the production of ammonia and other chemicals.

  Interesting from the point of view of feedstock flexibility is that the upstream visbreaker needs regular decoking, with a consequent change of feed to the gasifier. When the visbreaker is off line then the visbreaker feed (i.e. uncracked vacuum residue) is simply fed to the SGP unit. Like the units which purchase material in the open market, only minimal operational adjustments are required to accommodate such a switch of feeds 'on the fly.'

In reviewing experience in reference plants it may be of interest to look at maintenance requirements on critical equipment. Table 4 gives a summary of typical data.

Burners	
• Inspection intervals	~4 000 hrs
• Repair intervals	8 000 - 12 000 hrs
Refractory	
• dome repairs	~16 000 hrs
• wall	20 000 - 40 000 hrs
Waste heat boiler	
• coil inlet section	~60 000 hrs
Thermocouples	
• replacement intervals	2 500 - 8 000 hrs

Table 4: Typical Maintenance Data for SGP in Oil Service

Actual operating data for a single reactor operating in a four train environment over a 385 day period between annual turnarounds is described in Table 5.

Operating Period	**385**	**days**
Burner inspection/change	4	days
Change of thermocouples	1	day
Small disturbances, trips of upstream/downstream units	0.5	day
unplanned shut-downs	2	day
	7.5	days
On stream factor	98	%

Table 5: On-stream Factor for one SGP Train

5 Perspective for the future (or what next?)

As described previously a number of factors have led to a reevaluation of traditional extraction methods of carbon recovery, in particular the possibilities of recovering the vanadium for metallurgical use.

Looking at a typical visbreaker residue in a plant with a feed rate of 100 t/h, we see that 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 usable in the metallurgical industry, both the environmental issue and physical disposal can be simultaneously 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 3 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 an 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. The product is vanadium concentrate, which contains about 75% V_2O_5. The process is autothermal, the heat of combustion being sufficient to evaporate the moisture content of the filter cake.

The process is fundamentally simple, a fact which is reflected in a markedly lower capital cost than that of naphtha-based 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.

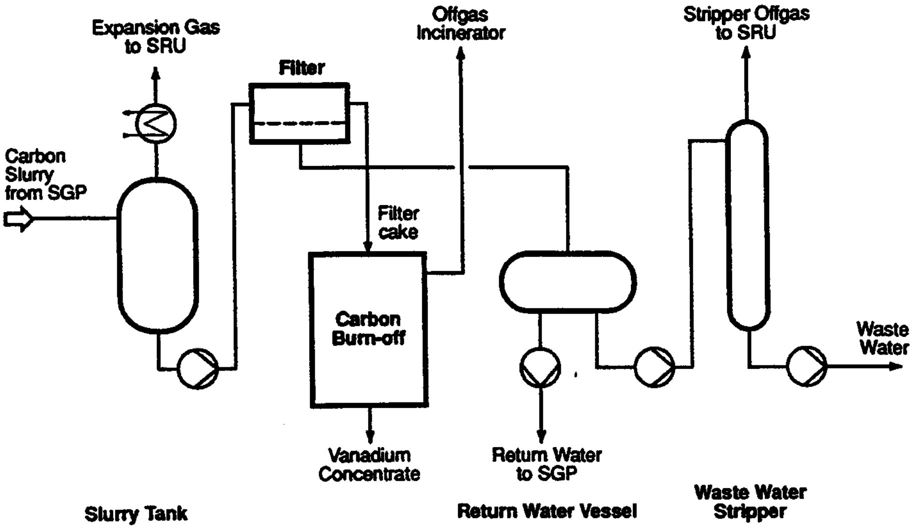

Figure 3: **Soot Ash Removal Unit**

An additional benefit of this development is increased feedstock flexibility, both for the SGP itself and for the refinery as a whole. The elimination of the carbon recycle allows one to use feeds with considerably higher ash contents than previously.

This type of carbon handling facility is being installed in SHELL's Pernis refinery at present and one can expect to see further refinements of this approach in the future.

6 Conclusion

Partial oxidation of heavy residues is becoming an increasingly useful building block in the refinery flow scheme. It is a process with a long history of reliable operation within the refinery context and is set to continue playing an important role in bottom-of-the-barrel processing.

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