

# **Gasify POX Soot for Reduced Costs**

**Christopher Higman, Siegfried Bajohr and Rainer Reimert  
Engler-Bunte-Institut, Universität Karlsruhe, Germany  
presented at the  
19th Annual International Pittsburgh Coal Conference  
Pittsburgh, 23rd - 27th September, 2002**

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Christopher Higman, Siegfried Bajohr, Rainer Reimert  
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## 1 Introduction

Improvements in the economics of power generation using the Integrated Gasification Combined Cycle (IGCC) over the last few years can largely be attributed to advances in gas turbine technology and, to a lesser extent, in oxygen production. Soot management downstream gasifiers processing refinery residues is identified as another area offering opportunities for savings both in investment and in operating costs. State-of-the-art processes for soot management are reviewed.

A research programme has been initiated at Universität Karlsruhe for the development of a new soot management process.

From the beginning it was recognized that any new system would need to cope with soot produced from plants handling a wide variety of gasifier feedstocks, so the project has included an investigation into the nature of the soot produced by various commercial gasification plants.

Post-gasification of the soot offers the opportunity to utilise the infrastructure of the main gasification plant to reduce equipment and operational costs. At the same time by producing synthesis gas it provides a solution to the off-gas problem present with soot slurry filtration based processes.

The present paper provides an interim report on the research project and reveals the potential for further development beyond the current programme.

## 2 Soot Production in Partial Oxidation Processes

In processes for the partial oxidation (POX or gasification) of heavy residues a certain amount of soot (or free carbon) is produced. The quantities generated vary from about 3 wt.% of the feedstock for older, medium pressure plants to between 0.5 and 1 wt.% in modern higher-pressure units. Despite the success in reducing the soot make over the years, it is recognised that it should not be reduced beyond a certain limit, which is essentially determined by the ash content or more specifically the vanadium content of the feedstock.

Most heavy petroleum residues contain some vanadium. The concentration of vanadium in the residue is dependent on both the quality of crude as well as the refining history of the residue. A typical visbreaker vacuum residue can contain as much as 400 ppm (wt) of vanadium.

It is known that vanadium, which under gasification conditions is present as  $V_2O_3$ , can deposit on the wall of a gasification reactor if there is an insufficient amount of soot to help sequester the ash out of the reactor. This  $V_2O_3$  has a melting point of about 1900 °C and does not as such present a problem. On shutdown, with the admission of air to a hot reactor or later during the heat up phase of a restart, the vanadium trioxide can oxidise further to  $V_2O_5$ , which has a melting point only of about 700 °C. In a quench reactor the  $V_2O_5$  may flow into the throat area and stick there where it can throttle the gas flow into the quench chamber, thus creating excessive pressure drop. In plants with a syngas cooler the risk is in the  $V_2O_5$  depositing on the heat exchanger surface reducing heat transfer and increasing pressure drop.

All known attempts at developing a "soot-free oil gasification" process have up to now failed because of these issues. Commercial partial oxidation processes have recognised this and have therefore developed various methods for handling this soot.

### 3 Soot Management

Whether operating with a water quench or a syngas cooler all commercial processes use a water wash to remove soot and ash from the synthesis gas. The development of soot management has therefore essentially been the development of soot slurry handling. Typically this soot slurry contains about 1% solids, i.e. soot and ash.

#### 3.1 Extraction processes

For many years soot management processes were based on the extraction of the soot from the slurry with a hydrocarbon [1]. The hydrocarbons used have varied from process to process. The principles were however similar and are illustrated in Figure 1.

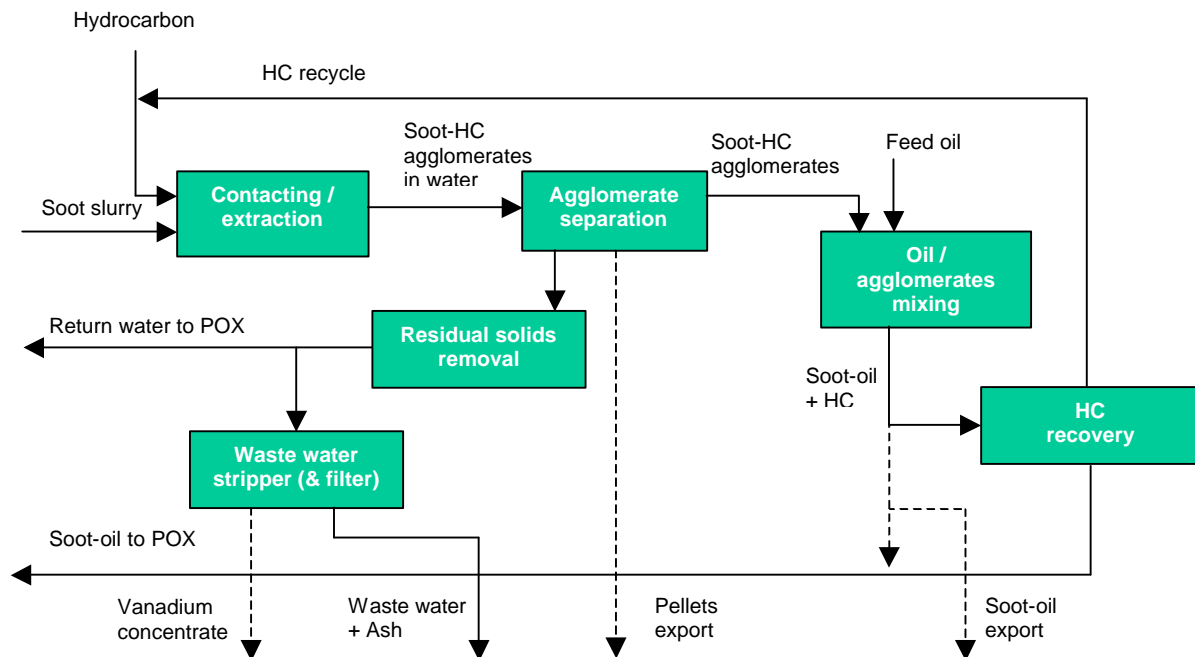


Figure 1. Generalised Extraction Process with Variants

##### 3.1.1 Extraction with Fuel Oil

One of the earlier forms of extraction process was the Shell Pelletising System (SPS). In this process the hydrocarbon used is a light oil, typically an atmospheric residue. It is contacted with the soot slurry in a stirred vessel. The soot together with most of the ash is extracted in the form of agglomerates (pellets) of a few millimetres diameter in a substantially but not entirely clear water phase (grey water). The pellets and the grey water are separated on vibrating sieves. In the simplest form of the process these pellets are used or sold externally and mixed with a solid fuel for firing. In a further development of the process the pellets are mixed with a heavier oil such as the main POX feedstock and either recycled in the form of a soot-oil mixture to the partial oxidation reactor or exported as a liquid fuel. Typically the export is to an auxiliary boiler within the gasification complex. The grey water is returned to the partial oxidation unit as wash water after removal of residual solids. As the overall water balance of the partial oxidation / soot handling system shows an excess, the waste is pre-treated by stripping out ammonia, hydrogen cyanide and hydrogen sulphide before discharge to a biotreater. The waste water also contains some of the ash from the feed.

This process has the advantage of a low capital investment but has a number of disadvantages, in particular in connection with the heavier feedstocks now considered standard for a partial oxidation plant.

- When exporting pellets for use as solid fuel, the price obtainable for the pellets tends to be below that of the pelletising oil contained. The pellets export therefore represents a permanent operating loss.
- The pellets are not free of water. If the feed oil to which the pellets are mixed is sufficiently heavy that a temperature of over 100 °C is required to obtain an acceptable pumping viscosity, then the water content of the pellets causes foaming in the atmospheric mixing equipment. This represents a limit to the application of the process.
- The bulk of the ash from the soot slurry is contained in the pellets and therefore in the soot-oil. A total soot-oil recycle is not possible since otherwise there is an unacceptable build up of ash in the circuit causing damage to equipment such as the feedstock charge pump, the burner and if installed the syngas cooler.

### **3.1.2 Extraction with Naphtha**

An alternative is to use naphtha as originally introduced by Texaco and then later also applied by Shell. The basic steps described above of contacting and extraction, agglomerate separation, oil / agglomerate mixing and water pre-treatment are essentially the same but operated under elevated pressure. The equipment required is therefore different in detail to take account of the pressurised design. But since naphtha is usually too expensive to use as a gasifier feed, an additional naphtha recovery stage is required as shown in Figure 1. The naphtha is recycled to the extraction stage.

In addition to the ability to use heavy feedstocks as the basis for the soot-oil, naphtha systems have the advantage of being more selective for the soot in the extraction stage. Much more ash stays in the water phase so that total recycle is possible with only moderate ash build-up. Furthermore the metals can be recovered from the waste water and sold as a concentrate to the vanadium industry.

Until about 1980 both fuel oil and naphtha extraction plants were built. With the increasingly heavier feedstocks being applied during the 1980's only naphtha systems were built, although details and equipment varied somewhat between different licensors.

### **3.1.3 Other Extraction Processes**

A number of other extraction processes have been developed, using e.g. toluene as extraction medium to generate carbon black from the soot slurry. The economics of these processes together with the variable product quality depending on POX feed quality have prevented commercialisation beyond single demonstration plants. These are therefore not discussed in any more detail here.

## **3.2 Processes with Soot Slurry Filtration**

Towards the end of the 1980's two developments led to a total rethink about soot handling. On the one hand it was clear that all developments towards an improved extraction process were highly capital-intensive. On the other hand the increased use of partial oxidation as an integral part of refinery bottom-of-the-barrel schemes led to more vanadium-rich material being used in gasifiers than previously.

A high vanadium content in POX-reactor feed was a recognised problem [2]. The threefold increase in ash content from plant feed to reactor feed in a typical naphtha extraction unit with total recycle only aggravated the situation further. In a publication reviewing aspects of the initial planning of the new Leuna Refinery in Germany it was pointed out that the vanadium throughput of the partial oxidation unit was 320 t/y [3]. Thus the focus was moved from the soot to the vanadium.

Filtration of soot slurry has already been practised at a number of plants but no other use than landfill had been developed. With higher contents of heavy metals in the feed, the filter cake had to be considered as hazardous waste with all the attendant costs, even as landfill. Nonetheless slurry filtration avoided the ash build up of the soot recycle and so offered a suitable starting point to overcome the vanadium problem.

The filter cake, although solid, still has a residual moisture content of about 80%, so that it clearly had no future as a fuel. But even incineration presented considerable problems. Any available incineration process operated at over 700 °C, the melting point of vanadium pentoxide. This material would foul heat exchanger surfaces and have a strongly corrosive effect on any refractory with which it came into contact. It was necessary therefore to develop a process, which took account of the properties of V<sub>2</sub>O<sub>5</sub> [4]. Two approaches to finding a solution were developed.

### 3.2.1 Multiple Hearth Processes

The flow diagrams of Lurgi's MARS process and Shell's SARU process are basically similar and will be treated here without differentiation. The process sequence is shown in Figure 2.

The soot slurry, which leaves the water wash with a temperature of over 100 °C, is cooled and filtered with a filter press or a band filter. The filtrate is, as in extraction processes, mostly recycled to the POX unit as wash water, the excess being discharged as waste water. The filtrate, when compared with the water from an extraction process, has the advantage that it is virtually solids free and no residual solids removal is necessary.

The filter cake has a residual moisture content of about 80%, irrespective of the type of filter. It is fed to the top of a multiple hearth furnace as conventionally applied in the vanadium industry. In the uppermost two stages, the cake is dried in counter current to the hot flue gas from the lower stages. In the lower stages the soot is subjected to a gentle roasting process, taking place at a temperature of around 650 °C. This low temperature combustion process ensures that the vanadium pentoxide formed in the process does not melt. The product from the bottom of the furnace contains about 75 % V<sub>2</sub>O<sub>5</sub> together with other metal oxides depending largely on the quality of the main POX feedstock. The remaining soot is typically 1-5 wt.%, which allows the ash to be sold into the vanadium industry as a raw material.

The flue gas from the furnace contains CO from incomplete combustion of the soot together with H<sub>2</sub>S and NH<sub>3</sub>, which are contained in the filter cake. There are a number of different approaches to handling this off gas, depending the configuration of other parts of the plant.

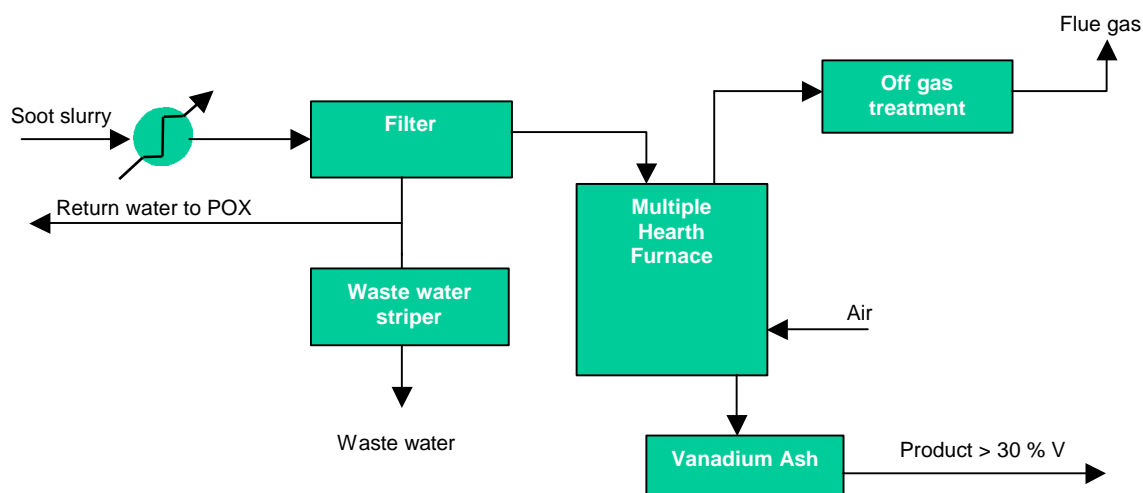


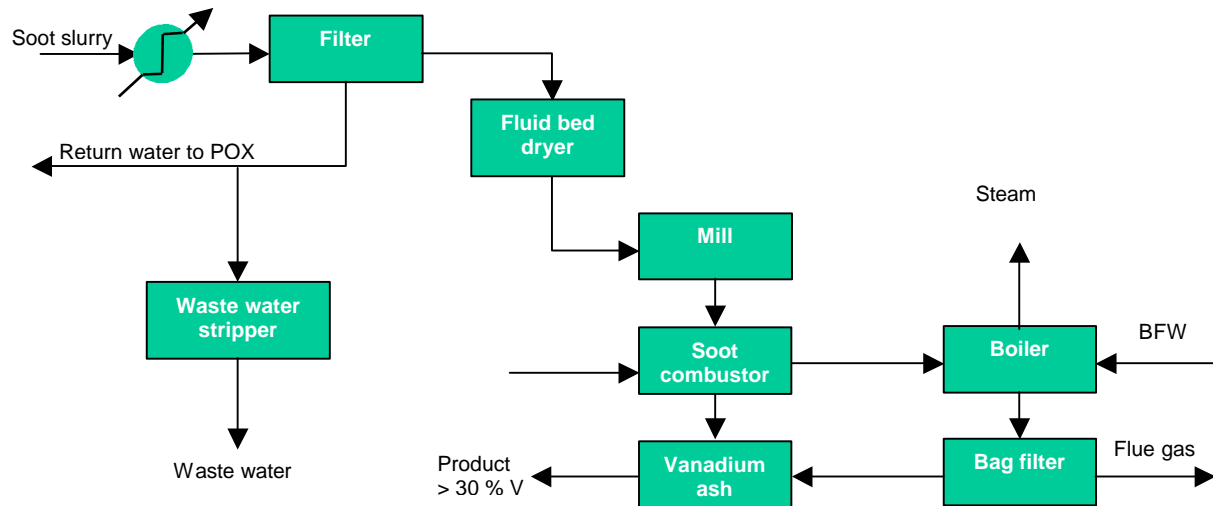
Figure 2. Generalised Multiple Hearth Furnace Process

### 3.2.2 The Norsk Hydro VR-Process

The Norsk Hydro VR (vanadium recovery) process, which has now been acquired by Texaco, is also based on soot slurry filtration and combustion of the filter cake. In this process however the filter cake is first dried and pulverised before being burned in a special cyclone combustor in which part of the vanadium is combusted to a liquid V<sub>2</sub>O<sub>5</sub>, which is then scraped from the combustion chamber floor. The heat of combustion is used to generate steam, which in general is sufficient to provide the necessary heat for the drying stage. Fly ash from the combustion

stage, which also contains  $V_2O_5$ , is collected in a bag filter and combined with that collected from the combustion chamber.

In the published flow diagram, which is more complex than shown here, there is no specific provision for sulphur recovery from the flue gas. Depending on circumstances this may have to be included. A fuller description of the process is available in the literature [5].



**Figure 3. Norsk Hydro VR Process**

### 3.2.3 Status of Processes with Soot Slurry Filtration

Both of the MHF processes and the NH VR process represent a considerable advance over extraction processes. In particular

- The avoidance of soot (and thus ash) recycle reduces the ash load on the feedstock charge pumps, the POX burners and the syngas coolers. This makes a significant contribution to an enhanced overall reliability of the plant.
- The lack of any ash build up in the circuit allows the gasification of residues with higher vanadium contents than possible when using an extraction process with soot recycle. This allows the processing of cheaper crudes in the refinery and is of considerable significance when processing some crudes from South or Central America with extremely high vanadium contents.
- Operating costs are lower than for an extraction plant. Compared with a fuel oil extraction, the loss through sale of fuel oil at solid fuel prices is avoided. The high cost of naphtha recovery is avoided when comparing with a naphtha extraction process.
- The capital investment is lower than for naphtha extraction.

Nonetheless there is still scope for further development of a more economic solution to the soot problem. Maule and Kohnke [5] and de Graaf et al [6] concur in this. However both concentrate on simplification of their respective processes. In particular they mention elimination of equipment considered necessary for inclusion in a first-of-a-kind unit, but which industrial experience has shown not to be required. Neither speaks of a change in the basic process.

## 4 The EBI Programme for a New Soot Handling Process

### 4.1 The Engler-Bunte-Institut of Universität Karlsruhe

The Engler-Bunte-Institut, named after Hans Engler und Carl Bunte, who worked on crude oil technology and gas manufacturing respectively, combines as a joint venture chairs of Universität Karlsruhe and the Research Station of the DVGW (Deutscher Verband des Gas- und Wasserfachs or German Association of Gas and Water). The Institute was from its inception a

cooperation between industry and the academic world and this has been an important strength over the whole of its nearly 100-year history. The first building for the Institute contained a pilot scale gas producer and this tradition of pilot plant work integrated with academic research continues to this day.

The Gas, Oil and Coal Division of the Institute today employs about 50 people. The current focus of research includes oil desulphurisation, carbon black production, gas based surface treatment of steels, biomass and other gasification processes, hydrogen purification for fuel cell use and Fischer-Tropsch synthesis.

## 4.2 New Concepts

The development of the filtration processes was based on the recognition that the behaviour of the vanadium in the ash is crucial to the oxidizing treatment of the filter cake. In particular the MHF concepts operate at low temperature specifically to prevent exceeding the melting temperature of the  $V_2O_5$  formed, which is about 700 °C. This low operating temperature, for all its benefits, has the disadvantage of a low reaction rate and thus high residence times and large equipment.

In the search for an improved process, it was therefore natural to look at higher operating temperatures with the accompanying reduced residence times. This can be done without moving to liquid phase  $V_2O_5$  only by operating with a low oxygen partial pressure to inhibit the pentoxide formation, in other words, to treat the soot under gasification conditions.

Apart from reducing the capital investment, this approach has the attraction of an elegant solution to the off-gas problem inherent in other filtration processes. The gaseous product of a soot gasification is synthesis gas rather than flue gas, so that the sulphur content is present as  $H_2S$  rather than  $SO_2$  and can be removed with conventional acid gas removal technologies, which are in most cases anyway present as part of the main syngas treatment facility.

Overall a soot post-gasification can be well integrated with the existing infrastructure of the main gasification unit, thus providing significant economies. This was confirmed in a preliminary economic study prior to embarking on the actual research programme. The study was based on the soot management for a plant to gasify 70 t/h of refinery residue. The soot gasifier has a diameter of about 2 m compared with a multiple hearth furnace of 5 m diameter. The installed cost figures show a 25 % reduction in the immediate filter cake handling section as well as the complete elimination of the off-gas incineration equipment. The operation cost for a complete soot management unit based on soot gasification was also shown to be lower, even if only marginally, than for either an extraction-based or a multiple hearth furnace-based unit. Since the naphtha extraction system involves recycle of the soot to the main resid gasifier, the comparison was made on the basis of total fuel and utility costs for syngas production in the main gasifier and the soot gasification (Table 1). These figures include supply of oxygen to the soot gasification and a credit for the heating value of the low-pressure syngas generated there.

Process	Naphtha-Extraction	MHF	Soot Gasification
Recycle rate	100 %	0 %	0 %
Operating cost €/1000 m <sup>3</sup> <sub>n</sub> (H <sub>2</sub> +CO)	16.49	15.83	15.79

**Table 1. Influence of soot management process on syngas production cost.**

### 4.3 The EBI Research Programme

One potential problem for any soot handling process is the wide variety in soot quality from a partial oxidation unit. Since the soot quality is essentially a function of the refinery crude quality and the subsequent refining history of the POX feedstock as well as of the actual operation of the partial oxidation process itself, this variation has to be accepted as a fact of life and any process must be able to cope with such variety to be successful. It was therefore decided that before any gasification trials with a particular soot, a wide variety of soots needed to be examined and characterised. Some of the results of these investigations have already been reported [7].

Secondly, in order to prepare the pilot plant it was necessary to develop an expected range for the gasifying conditions and any filter cake pre-treatment for the trials. This looks at factors such as further drying after filtration, the gasifier feed system, as well as temperature, pressure, flow regime and particle size in the gasifier.

Only after consideration of all these factors is it possible to go forward to the next stage, namely operating the pilot plant with a commercial soot feed.

#### 4.3.1 Process Configuration

In developing a target operating window for soot gasification it was realised that the usual criteria for optimisation of POX-processes were entirely inappropriate. The unit processes a waste material, which is only about 1% of the total feedstock. The quantity of syngas produced is of the same order of magnitude. Thus the yield of  $H_2 + CO$  per unit of feed is not decisive in the manner it is for the main POX unit. On the other hand two other criteria are of considerable importance.

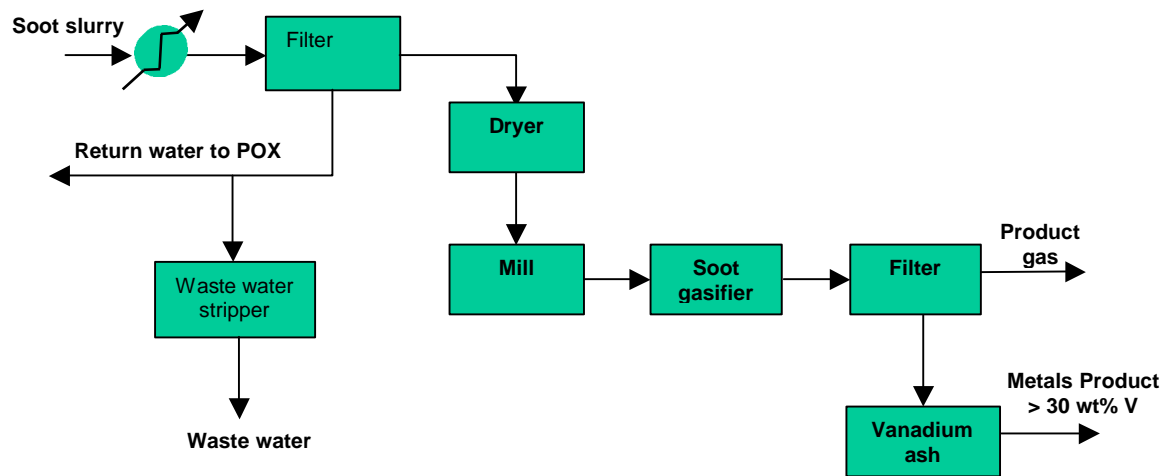
- A low carbon quantity in the ash is required to make the latter saleable to the vanadium industry. This clearly directs the choice of reactor toward the entrained flow type.
- Furthermore a low capital investment is desired. Operation at near atmospheric pressure will avoid the cost of pressurising the filter cake feed.

The operating temperature will have to be chosen to optimise the ash quality after completion of the test programme.

Syngas cooling also has to be considered. For a unit supporting a large POX with 70 t/h feed, steam generation will remain below 1 t/h. Under these circumstances it makes no economic sense to install a steam generator. The two realistic alternatives are boiler feed water preheat for the main unit or a direct quench. Attention must also be given to the potential for  $V_2O_5$  depositing on the cooling surfaces. A number of strategies for addressing this problem are currently under review.

Finally a decision will need to be taken on pre-treatment of the filter cake prior to gasification. Although the moisture content from band filters and filter presses is similar, about 80 wt.%, the filter press cake is harder and could be ground without drying. This has however process consequences. Gasifying with 400 % water to dry matter produces a syngas with 13 - 14 mol%  $CO_2$  compared with around 4 mol% when gasifying with a feed containing only about 50 % water to dry matter. The oxygen demand would also increase by 14 %. But remembering the context of the overall POX unit, this increase is actually only 0.14 % of the total oxygen production. This alternative is therefore not unattractive and some of the current work involves looking at transport and handling properties of an undried soot. A block flow scheme of the targeted configuration is show in Figure 4.





**Figure 4 Proposed EBI Process**

#### 4.3.2 The EBI Pilot Plant Gasifier

The next stage of the programme is the performance of actual gasification tests with oxygen blast in the EBI pilot plant in Karlsruhe.

The pilot plant facility includes a 70 mm entrained-flow gasifier, which has played a key role in the EBI's biomass gasification programme [8, 9 and 10] and will also be used in the current soot management programme. (See Figures 5 and 6).

Operation parameters for the biomass programme extend to 1300 °C and 1.4 bar.

As can be seen from the flow diagram, the installation includes a candle filter using high temperature ceramic candles for gas cleanup.

Initial operation of the pilot plant has commenced and first results are expected during the course of the next few months.



**Figure 5 70 mm Entrained-flow Gasifier at EBI**

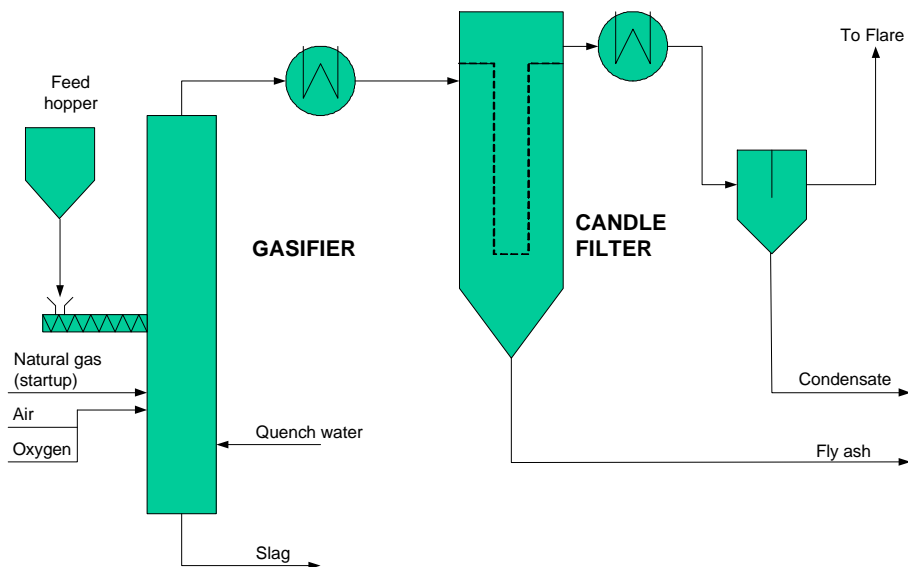


Figure 6 EBI Gasifier Installation

## 5 Potential Syngas Applications

The gaseous product of the proposed process is a raw synthesis gas, which is suitable for several applications. Since the gas is produced at low-pressure the obvious use is as fuel gas. In many refinery applications, the gas would not need to be desulphurized, since it would displace a fuel oil with a higher sulphur content than the gas. If desulphurisation is required, then this could be effected by a side stream of the main syngas acid gas removal (AGR) system. In such a case this can be achieved at minimal cost, remembering that this gas stream represents less than one per cent of the total AGR design load.

An alternative route would be to recover the gas as syngas for the main product stream. Recycling to a location upstream the AGR would ensure that subsequent gas treatment would simply be part of the main process. Thus the carbon in the soot would be totally recycled to the process without burdening charge pumps, burner and syngas cooler with an additional ash load. The cost of recompression is however likely to make this solution unattractive except in special circumstances.

## 6 Future developments

The current development programme is expected to bring an improvement to the economics and the operation of soot handling systems in partial oxidation units. It is however also worthwhile looking beyond this programme to see what scope there is for additional advances in this area. One, which comes to mind, is the potential for dry filtration of the soot from the gas. This is a normal unit operation included in many coal gasification plants. There is no principle reason why it should not be applied to syngas in oil gasification units. The difficulty in the past has been the nature of the dry soot product, which is "fluffy" and difficult to handle. The current development offers for the first time the possibility of processing the soot from a dry soot filter. This has a number of advantages such as

- Elimination of much of the water circuit in existing POX units. (The excess water deriving from process condensate would still be there, but free of its solids load.)
- Elimination of the filter press, which in the present scheme remains an extremely costly item.

- The possibility to recover the soot and operate the soot post-gasifier at an intermediate pressure, thus reducing syngas recompression costs to an acceptable level for gas recycle.

## **7 Conclusion**

Handling the soot from the partial oxidation of heavy residues is a cost burden for gasification, which has not yet been solved. A research programme to develop an optimised process is in place at the Engler-Bunte-Institut of Universität Karlsruhe based on post-gasification of the soot. Initial estimates give reason to anticipate significant cost savings. The process route under investigation also offers potential for further development beyond the scope of the present programme.

## **Acknowledgements**

Thanks are due to those companies which have provided the soot samples, without which this work would have been impossible and also to Lurgi Öl Gas Chemie GmbH who have sponsored part of the investigations reported

## References

- [1.] Brejc, M., in Ullmann's Encyclopaedia of Industrial Chemistry, 5. Edition Vol. A12, p. 209
- [2.] Soyez, W., "Slag-Related Risks in Partial Oxidation Plants", AIChE Ammonia Safety Meeting, Denver 1988
- [3.] Heurich, H., Higman, C., "Partial Oxidation in the Hydrogen Management Scheme", AIChE Spring Meeting, Houston; March 1993
- [4.] European Patent-No. EP 0542322, "Method for Treating a Vanadium containing Residue"; 28. September 1992
- [5.] Maule, K., Kohnke, S. "Technical, Economic and Environmental Improvements at Hydro Agri Brunsbüttel, The Solution to the Soot Problem in an HVR Gasification Plant"; GTC-Conference, San Francisco, October 1999
- [6.] De Graaf, J.D., Zuideveld, P.L., van Dongen, F.G., "Shell Pernis Netherlands Refinery Residue Gasification Project", IChemE Conference "Gasification for the Future", Noordwijk, Netherlands, April 2000
- [7.] Higman, C., Bajohr, S., Reimert, R., "New Developments in Soot Management", IChemE Conference "Gasification – The Clean Choice for Carbon Management", Noordwijk, Netherlands, April 2002
- [8.] Roll, H., "Vergasung von grob gemahlenem Schilfgras (*Miscanthus Sinensis Giganteus*) im Flugstrom", Doctoral Dissertation, Engler-Bunte-Institut der Universität Karlsruhe, Bereich Gas, Erdöl und Kohle, 1994
- [9.] Bajohr, S., "Reaktionskinetische Untersuchungen zur Umsetzung von Naphthalin und Benzol an Koks in einer H<sub>2</sub>- und H<sub>2</sub>O-reichen Atmosphäre", Dissertation (Diplomarbeit), Engler-Bunte-Institut der Universität Karlsruhe, Bereich Gas, Erdöl und Kohle, 1996
- [10.] Klensch, S., "Verhalten von Schwermetallen bei der thermischen Umwandlung von Sägespänen im Flugstrom", Doctoral Dissertation, Engler-Bunte-Institut der Universität Karlsruhe, Bereich Gas, Erdöl und Kohle, 2001

This text is published in the Proceedings of the 19<sup>th</sup> Annual International Pittsburgh Coal Conference