

Initial Operation of the Shell Pernis Residue Gasification Project

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Summary

The successful start-up of the PER+ project, a major revamp of the Shell Pernis refinery, is described. The heart of the new project is a world scale hydrocracker supplied with hydrogen by Shell Gasification Process units processing very heavy refinery residues. Significant amounts of electrical power are also generated from gas- and steam turbines. These units allow the Pernis refinery to process an expanded range of crudes producing more high quality products at a lower environmental impact. The plant was in full operation early 1998.

Introduction

The Shell Gasification Process, SGP, is an efficient and environmentally benign process for converting heavy refinery residues into clean products. In the Shell Pernis refinery this process has been made part of a major refinery revamp. In this project (called PER+) the Shell Gasification Process is the key element in converting very heavy refinery residue into hydrogen and clean fuel gas for power.

The Shell Pernis refinery revamp, PER+

Shell Pernis is one of the largest industrial complexes in the Netherlands. Two independent companies operate at the site: Shell Nederland Raffinaderij B.V. and Shell Nederland Chemie B.V. Refinery activities began at the current site in the early 1930's, and today's refinery is highly complex with a capacity of about 18 MMt/yr (400 000 bbl/d). A strategic study was started in the late eighties for the period into the next century. With a lower USD/NLG exchange rate resulting in higher dollar cost, ageing facilities, tightening environmental requirements and product quality specifications a step change was required to provide a sustainable future for the refinery. The age of the existing units also played a role here: cat-cracker #1 was over 45 years old and modification of this unit to comply with environmental legislation would be questionable. This resulted in a refinery rejuvenation project (PER+) in which the Shell Gasification Process plays a major role. The project centred around the integration of the following units:

- a world scale hydrocracking unit of 8000 t/d throughput with a hydrogen consumption of 285 t/d;
- a 1650 t/d residue gasification unit for the production of both the hydrogen for the hydrocracker and clean fuelgas for a co-generation power plant.
- a co-generation power plant comprising two gas turbine- (GE frame 6) and two steam-turbine generator sets that consume the clean gas from the gasification not needed for the production of hydrogen as well as all the steam generated in the effluent boilers of the gasification.

As part of this 3.2 billion Dutch guilders project several more new facilities were realised for: water demineralisation, amine regeneration, sulphur recovery, sour water stripping, product manifolding, etc. requiring over 8000 tie-ins.

Construction started in 1993 and the full project was completed by the end of 1997. Construction, (pre)-commissioning and start-up was achieved within a tight budget and time frame. No refinery upsets or environmental incidents occurred. With the whole project completed the above mentioned three key installations are now part and parcel of the overall refinery process, see Fig. 1.

Shell Gasification in PER+ for hydrogen manufacture

For the new hydrocracker a significant amount of hydrogen is needed. Although hydrogen rich off-gas from a catalytic reformer currently used as refinery fuel could be freed by replacing it by natural gas, new capacity

was needed. Steam methane reforming of natural gas was considered as an alternative (SNR already operates one SMR plant for Hycon). However, for this extension a process based on Shell Gasification was selected since it reduces high sulphur fuel oil production, enhances the crude oil flexibility of the refinery, while at the same time the refinery environmental fingerprint could be greatly improved, see Table I.

For the Pernis project thus a hydrogen plant based on the Shell Gasification Process was developed, it is named: Shell Gasification Hydrogen Plant, SGHP. Since this SGHP was to play a key role in the new refinery configuration an obvious requirement for the design was, to base it on proven technology. Still, as a result of prudent risk taking, some new features in the configuration and the design of the down stream hydrogen manufacturing section were chosen, the most important one being the application of a low temperature shift at relatively high pressure. Also a new system for the handling of the gasification soot and ash was developed, called Soot Ash Removal Unit (SARU).

The SGHP has the following configuration, see also Fig. 2.

- Gasification.

The gasification is done in three parallel trains with a total capacity of 1650 t/d residue, either vacuum flashed cracked residue from the thermal cracking unit or a mixture of straight-run vacuum residue and propane asphalt. A larger gasification capacity is installed than required for the hydrogen production proper, the excess syngas to be used as a clean fuel for the gas turbines of the new co-generation power plant. Also other effluent streams from the down stream gas treating unit in the SGHP are admixed to this excess syngas. The capacity of the strings is chosen such that the hydrogen for the hydrocracker can be produced by two gasification strings only, the maximum being 285 t/d. Each train consists of feed pumps, a reactor-effluent boiler combination, boiler feed water preheating, soot-quench and soot-scrubbing. The gasification is performed at about 1350°C and 65 bar. The product of the partial oxidation reaction is a raw synthesis gas which contains particles of soot and ash; typical values are around 0.5 %wt. on feed. The recovery of the high quality sensible heat contained in this gas is an integral feature of the SGP process. The raw gas is cooled to below 400°C and the heat recovered produces high pressure steam at about 95 bar. This pressure level is set to match that of the heat recovery steam generators down stream of the gas turbines. In this way the saturated steam from the SGP effluent boilers can be superheated in the power plant and used for power generation. The effluent cooler is of standard design: it is applied world-wide in all SGP installations. Residues originating from all crude oils known to Shell can be gasified in the SGP without resulting in serious fouling or corrosion/erosion of the coils of this effluent boiler. After the boiler the raw gas is passed through an economiser where boiler feed water is heated from 140 to 200°C, before reaching the soot quench for particulate removal. Next raw gas passes through a cooler before entering the scrubber. After leaving the scrubber at a temperature of about 40°C the gas has a residual soot content of less than 1 mg/m³ and is suitable for feeding to the de-sulphurisation unit.

The oxygen required for the gasification is supplied via a pipeline of about 8 km at approx. 70 bar and 99.5 %v purity from a new air separation plant owned and operated by Air Products. No compression is done on the Pernis refinery site.

The gasifier is equipped with a proprietary co-annular burner, with integrated reactor heat-up and hot standby operation. The unit is equipped with a fully automatic start, stop and safeguarding management system. The residue feed, oxygen and steam are fed by ratio control to the burner. For the feed control to the gasifier the conventional concept of using the reciprocating feed pumps as flow measuring device was selected, however, for safeguarding independent flow information is required and for this a coriolis type of device has been installed in the residue feed line to the burner. This coriolis flow measurement was specially developed for the Pernis operating conditions (high pressure and high temperature) and was tested first in Pernis in a similar service.

- Sulphur removal.

For the treating of the raw syngas the Lurgi Rectisol process was chosen. This is a one string unit that integrates sulphur removal with the CO₂ removal down-stream the CO-shift. Here deep sulphur removal takes place for the feed to the CO-shift unit, dictated by the application of a copper based catalyst in the low temperature shift. The excess syngas for GT fuel, however, is taken as a side stream from the main absorber at a slightly lower purity. Low pressure off-gases generated here are also routed to GT fuel. The

Rectisol is a low temperature process, even though a major share of the required cold is generated by the desorption of CO₂ additional cooling power is required. For this a propane cycle is chosen.

- CO-shift conversion.

The de-sulphurised syngas is shifted in two steps to a residual CO level of about 1 %v (dry). The first stage (HTS) is at high temperature, in a Lurgi reactor. For the second stage a copper based low temperature shift system (LTS) is selected. For this reason the de-sulphurisation in the Rectisol must be very deep indeed, still, for final S removal, a ZnO bed is installed upstream the LTS. Notwithstanding the deep S removal the LTS cat life is expected to be somewhat less than is normal for LTS catalysts in steam reforming applications. A second LTS reactor is installed allowing for on-line catalyst change without plant shutdown.

- Carbon dioxide removal.

After the CO-shift a full CO₂ removal is done, again with Rectisol, this section is integrated with the H₂S Rectisol. Regeneration of the solvent is by means of sequential flashes, the last one sub-atmospheric. Since the off gases from the first flash stages contain co-absorbed hydrogen these streams are also being used as gas turbine fuel components. The majority of the CO₂, about 3000 t/d, however, is being released directly to atmosphere. To minimise methanol emissions (150 mg/m³ is a limit) prior to venting the CO₂ is subjected to a water wash. Recently the refinery has started negotiations for the potential use of this CO₂ in nearby greenhouses.

- Methanation.

Residual carbon oxides are converted in a catalytic methanation reaction yielding hydrogen well over 98% purity by volume with a pressure of about 47 bar.

- Soot and ash handling.

The Soot Ash Removal Unit (SARU) was developed in 1991 as a new, more environmentally friendly and economic method of soot/ash removal for gasification. The application of SARU makes the soot processing not only environmentally acceptable but also disconnects it from the main stream of hydrogen and power generation, thus increasing the reliability of the overall process. It also avoids the build-up of ash in the gasifier feed, as is the case with recycling processes. This means that the Pernis refinery gets an additional flexibility in its crude diet, since any residue it produces can be processed. Since the SARU is not a recycling process that should be closely linked to the gasification, it can be treated as a separate plant. For several reasons it was located in a different area of the refinery, at some distance from the SGHP. Consequently it is also operated from a different control room. Even though the unit operations in the SARU by themselves are well proven, the integrated unit in relation with gasification is new and did pose some risk. For that reason, in this first SARU, major attention was given to the reliability inter alia by sparing of equipment and building in over capacity.

The soot formed in the partial oxidation reaction is removed from the system with the process condensate as a soot slurry (1% wt. carbon on water) and is routed to the SARU. After soot removal the water is returned to the soot scrubbing section, excess of water is routed to the waste water treatment section.

The soot and ash are filtered out of the slurry using an optimised filtration method producing a hard filter cake with about 20% wt solids and a clear water filtrate. Advanced process controls are in place to handle the transitions between continuous SGP and discontinuous filtration. This system can also handle about three hours disruption of filter press operation.

The filter cake is subjected to controlled oxidation in a multiple hearth furnace (MHF). This furnace yields a metals oxides ash with a minimum of residual soot and thus high metal concentrations, Vanadium oxide typically around 65%. The ash is a marketable product and not a waste material; Pernis has a sales contract with a metals reclaimer. Utmost care is taken with the handling of this ash, because of the toxicity of the vanadium- and nickel oxides.

Off gases from the combustion pass through dust removal equipment and a CO after-combustion step. In this way the SARU in Pernis complies fully with the environmental constraints set by authorities in the permit to operate the refinery.

The Co-generation Power Plant.

As integral part of the PER+ project a new Co-generation Power Plant was constructed. This unit serves as the major utility centre for the refinery, producing electrical power, steam for refinery operation (including for the SGHP), boiler feed water, instrument air, etc. The heart of the unit is formed by two GE MS 6541B gas turbines with two heat recovery steam generators (HRSG) and two steam turbine sets. The gas turbines can operate on syngas, on a mixture of syngas from the SGHP with LPG and/or natural gas as well as on natural gas alone. NO_x emissions from the turbines is controlled by steam injection. The steam generated by the gasification effluent boilers is directly fed into the steam drums of the gas turbine HRSG's and subsequently all generated steam is superheated and passed to the steam turbines. Here power is produced as well a superheated steam for the refinery. The steam turbines also can accept medium- and low pressure steam from the refinery when this is available in excess.

Start of the SARU

As said above, the Soot Ash Removal Unit can be seen as a separate unit. Since it was situated in a different area its construction was advanced such that the unit could be tested far before the actual start of the gasification section. The final testing was done with soot filter cake and soot water imported from SGP licensees. In this way several problems were identified and successively solved. Although some problems could only be solved after the start of the first Pernis SGP, the unit never was a constraint to the overall operation.

Areas that required special attention during the first operational period were:

- Filtration. During the initial testing bugs in the logic for the operation of the filter-presses were encountered and successively removed.
- The MHF temperature control. The furnace has a fully automatic temperature control. A very tight temperature control was applied to avoid producing large lumps of slag or liquids corrosive to the refractory from the vanadium oxides. Setting of this control could not be sufficiently predicted in the test facilities, and tuning had to be done on the spot.
- The dust recycling system. Dust that carried over from the MHF, and that was separated by cyclones and dust filters could initially not easily be returned to the furnace. As it turned out the nitrogen purges on the rotary valves employed hindered the flow of dust. This was solved.
- Filter bag house. To bring the dust emission level of the SARU down to below 50 mg/m³ a bag house is installed downstream the furnace. The measurement of the dust level in this bag house has been modified so that dust recycling problems here could be solved as well.
- CO afterburner. To bring the CO levels of the SARU down below the mandatory levels of 10 mg/m³ a CO combustion step was installed. A special low NO_x burner was installed which brought the NO_x level from the SARU down to a low level. This burner, however, initially gave rise to humming that damaged the refractory in the top of the incinerator. This problem has now been solved.

After solving the start-up problems the SARU is operating very well, shipment of the first parcel of ash awaits clearance from the authorities.

Start of the Power Plant

Superheated steam needed for the gasification and hydrogen manufacture is generated by the new power plant. This unit therefore had to be in operation first. Both gas turbines were started on natural gas early in 1997. The starts and subsequent operation were excellent. Difficulties with steam valves, vibrations and noise at steam let-down stations delayed the moment of production of reliable steam, however, these have been overcome in time.

Introduction of steam from the SGP effluent boilers went very smoothly and has never given any problems. The first feeding of syngas from the gasification to one of the gas turbines (the other was kept on natural gas) turned out extremely well. Apart from some minor control problems in the gas manifold no difficulties were encountered.

Start of the SGHP, first operational experiences.

The gasification plant in PER+ is the first application of heavy residue gasification fully integrated in a refinery operation. Since the success of the whole project and therefore the future of the refinery hinges on this unit also for this plant quite some effort was invested in maximising the chance for a successful start. Extensive cleaning and testing was performed thereby accepting a possible later start of the facility. In the whole complex special attention was given to plant cleanliness and tightness of valves and flanges. Certainly the latter was very successful owing to an extensive program of hydraulic bolt tensioning and training of personnel on this subject. During the commissioning of the gasification the cleanliness of the feed system, especially the oxygen section and the valves in the automatic start/stop/safety interlock system were the major areas of attention.

- The oxygen supply line.

The supply of the oxygen is under about 70 bar pressure. The dedicated line from the new, Air Products oxygen plant to the metering station on the refinery site is carbon steel as is the underground transmission line from the metering station to the three gasifiers. Just prior to the admission of oxygen the off plot line was frequently blown and finally target blown with nitrogen. The in-plot line was thoroughly chemically cleaned, this was repeated until confirmation of cleanliness with TV camera inspection. A hindrance here was an insufficient slope of this underground line. The lines were subsequently put under oxygen and slowly pressurised to the full pressure. No adverse effects like temperature rises were observed.

- Gasifier start-up/shut-down logic.

Each gasifier is governed by a dedicated PLC that supervises the heat-up, start-up and shut-down sequences and safeguarding. The full sequences were extensively tested in the field with the actual equipment. In this the oxygen was replaced by high pressure nitrogen, supplied through the full oxygen supply grid from the Air Products site. Residue feed was simulated with high viscosity lube-oil that by means of a temporary by pass over the burner was returned to the feed vessel.

The auxiliary heat-up burner was tested outside the reactor on natural gas and air. As a result of this extensive testing starts of the gasification reactors have been very successful. During the first starts only a minor tuning of the controls to the dynamic behaviour of the full system had still to be made. The largest of these related to the dynamic behaviour of the steam supply during an upset in the power plant.

- Valves in oxygen service.

During the testing of the control and safeguarding logic problems with valves were encountered. These had to do with the accuracy of the proximity switches on these valves. This was solved and as a result of this effort only an occasional spurious trip has occurred.

- During heat-up with the effluent boilers severe steam hammering was experienced. Since the design of the effluent cooler is applied numerous times over this was not expected to happen. It was found that in this particular Pernis configuration a combination of warm-up steam sparger design and heat-up procedures applied was the cause. The problem is well understood and has not recurred after modifications of the sparger and the operational procedures.

The first start of the first gasifier was in mid October '97 and by the end of that month the first hydrogen was produced. The second gasifier was started directly after this. The steam produced by the SGP effluent boiler then already was processed in the power plant.

A description of the automatic start of the gasifier is noteworthy. The reactor is being heated to starting temperature with natural gas and air with the main burner. Upon reaching the starting temperature the condition is held as long as needed to have the steam, oil and oxygen systems lined up ready for the start. When the systems are ready the operator can initiate the start from the panel. There is then no operator action outside needed; no burner exchange required. Then about 10 minutes after the initiation of the start the unit is operating steady at about 65 bar and 70% capacity. As an example the dynamics of the first start a gasifier is shown in Fig. 3. Because of the method of control of the start and stop of a gasifier no adverse affects on the operation of other gasifiers were encountered.

In case of a plant stop or trip the system automatically brings the unit back in a situation that the operator can restart the heat-up mode on natural gas/air, also then no re-installation of a heat-up burner is required.

To test for the first time the gasification reactor line for potential flange leakages, for example from stresses at the high operating temperatures, the whole gasification section was pressure tested integrally at about 50 bar with nitrogen when the reactor was heated to well above 1000°C. The heat-up was temporarily interrupted for this. The burner flange could also be tested at this moment, since the burner did not have to be removed anymore. After the pressure test heat up was resumed. No leakages were detected, this was later confirmed after the start.

Within hours after the start of the first gasifier the raw synthesis gas was passed to the downstream Rectisol de-sulphurization section. Preparation for the start of this section (in conjunction with the CO₂ removal section) was done by an extensive commissioning with water. Only after this the solvent was put in the unit and cool down of the unit started. As a consequence of this and the successful hydraulic bolt tensioning program the admission of synthesis gas to the Rectisol went relatively smooth, particularly no leakage of the low temperature flanges.

The performance of the CO-shift section was as expected; especially the low temperature CO-shift catalyst deserves commendation: it proved to be as good as predicted from laboratory tests. Major attention here went to the vortex- and ultrasonic flow measurements.

Early 1998 the full SGHP was on line and producing hydrogen and syngas for the gas turbines on demand, i.e. following the hydrocracker and power plant. The plant fully meets the high degree of reliability demanded for this type of operation.

Table I

Environmental impact PER+ investments

Refinery mass balance, MMt/a		
In:		
HS crude	11.3	15.0
LS crude	4.5	2.8
Other feedstocks	2.1	0.1
Total intake	17.9	17.9
Out:		
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
Crude oil properties		
Average API-gravity	32	31
Average S-content, %wt	1.55	2.3
Sulphur balance, MMt/a		
Sulphur in crude and feedstocks	0.28	0.41
Sulphur recovery	0.11	0.30
Sulphur in all products	0.15	0.10
Sulphur emissions	0.02	0.01
Sulphur recovery, % on S intake	28	73
Refinery emissions, kt/a		
SO ₂	35	24
NO _x	12	7
Particulates	4.0	1.9
Total emissions, refinery + products		
SO ₂ , kt/a	348	206
CO ₂ ,	56.6	56.8

Shell Gasification in Pernis

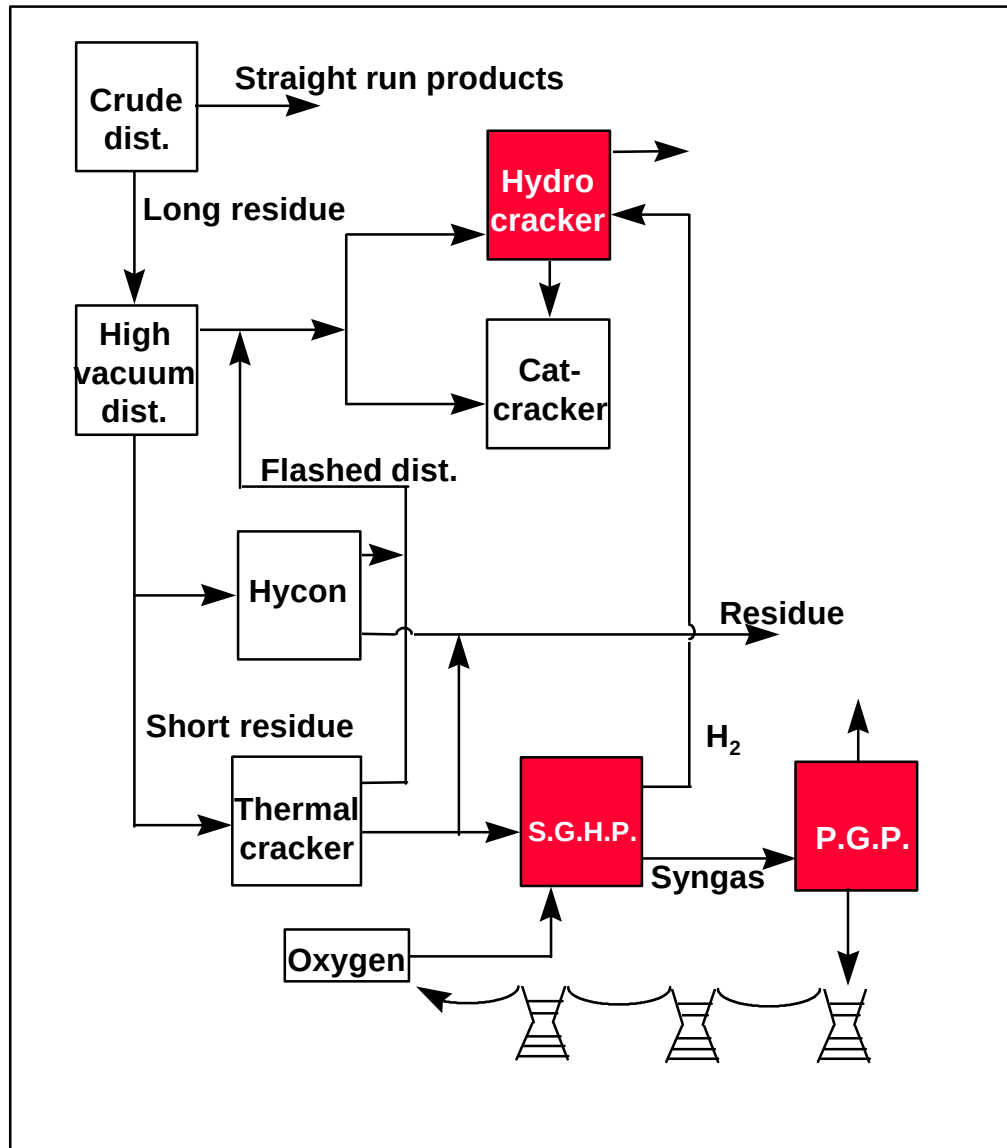


Fig. 1
Pernis Refinery configuration

Shell Gasification in Pernis

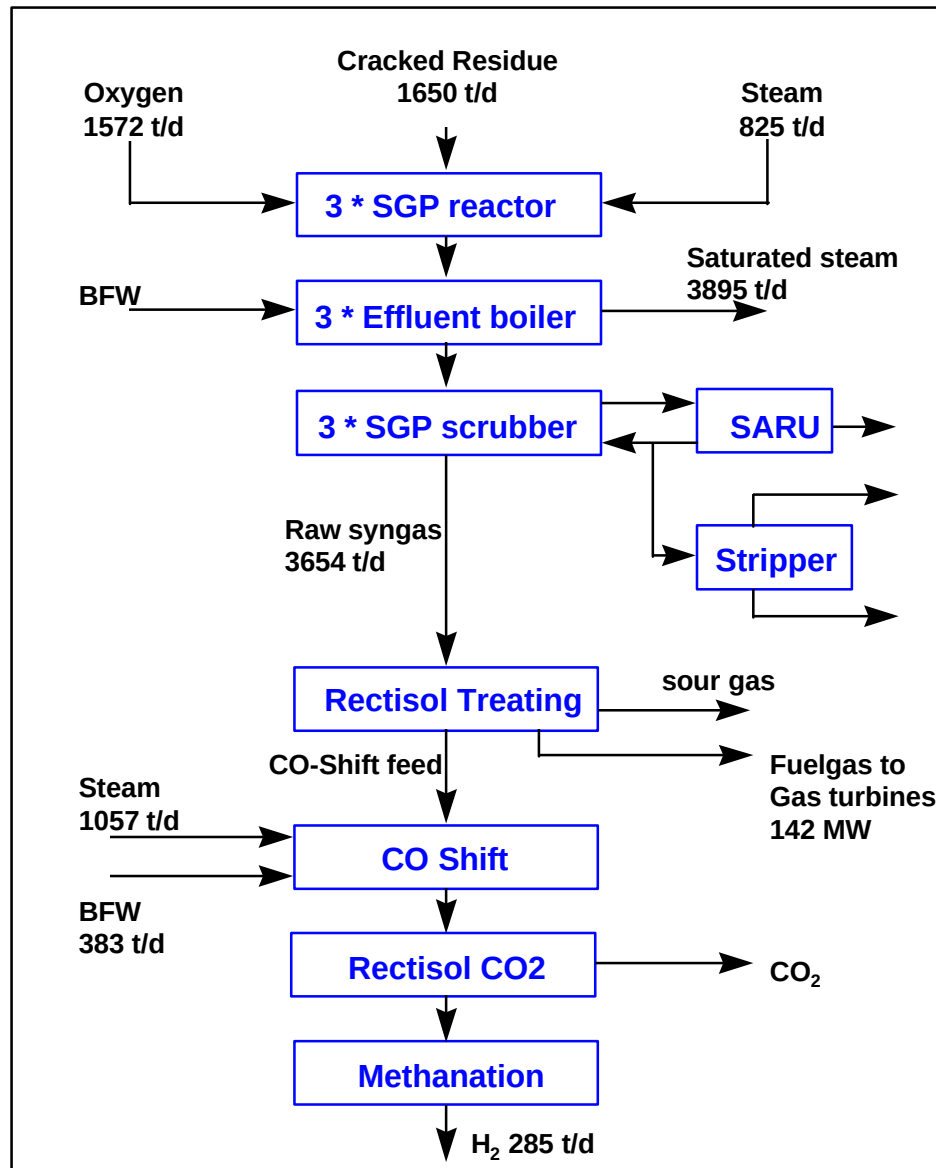


Fig. 2
Configuration of SGHP

Shell Gasification in Pernis

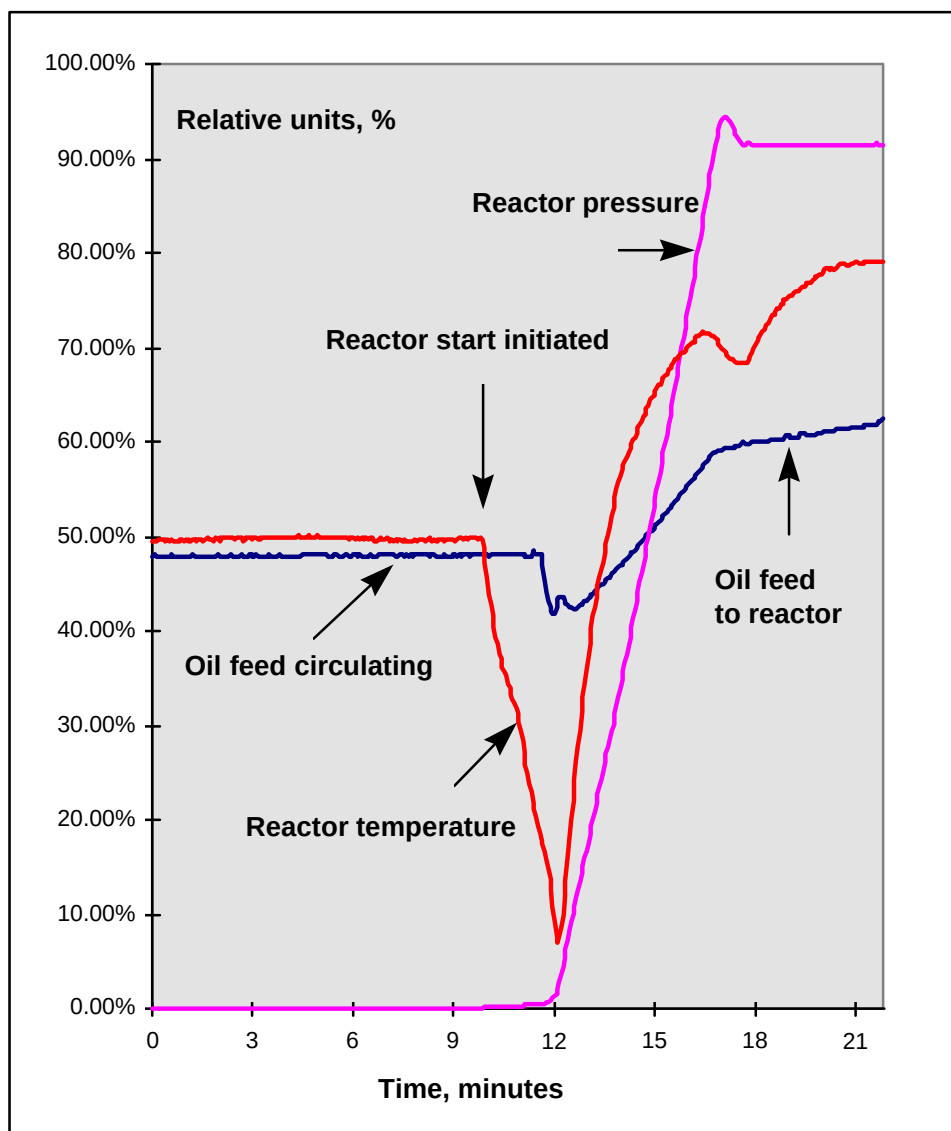


Fig. 3
SGP start