Gasification of Residue as a Source of Hydrogen for Refining Industry in India

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Abstract

The increasing demand of clean fuel products going along with a tendency of growing heavier crude oil availability and petroleum coke will force many refineries to further reduce the bottom of the barrel by changing the basic configuration of the refineries.

The Clean Fuel Act in the United States, the Auto Oil Programme in Europe, and numerous similar legislation efforts as a part of the new definition of automotive fuel quality around the world, including India, are causing drastic limitations for sulphur and aromatics. Especially these two parameters will change the internal hydrogen balance of the refineries because of their counter-current effect. The deep desulphurization of various fuel streams requires more hydrogen and the reduction of aromatics will lead to less hydrogen surplus from catalytic reforming due to low severity operating conditions.

In such a situation the catalytic reforming as the major source for hydrogen in refineries will not be sufficient anymore to satisfy the growing demand for hydrogen. Consequently, two options for hydrogen production are becoming more important. Steam reforming of light hydrocarbons, natural gas or LPG which is used to produce the bulk of hydrogen today or partial oxidation of residues or even petroleum coke.

The disadvantage of the relatively higher investment for a gasification unit compared to steam reforming will be compensated for several reasons described hereinafter, whereas one of those is the search for the best techno-economic way to dispose of refinery residues.

In this situation gasification offers a very versatile process for the conversion of even the heaviest “bottom of the barrel” refinery residues into clean synthesis gas, which can be used to produce hydrogen, power, fuel gas or steam for any refinery purposes as well as gases for the chemical industries.

Shell Global Solutions International B.V. with Krupp Uhde as the authorised engineering partner offers two fully proven gasification technologies - Shell Gasification Process, SGP, for gaseous and liquid feedstocks and Shell Coal Gasification Process, SCGP, for solid feedstocks.

The paper describes several alternatives for hydrogen production for the Indian refining industry.
1. Introduction

The growing demand for lighter and cleaner fuel products, the heavier crude oil sources for the refineries and the economical situation inside the refineries to downgrade the bottom more and more is changing the configuration of the refineries.

Besides the globally increasing demand for hydrogen, the refineries are looking for the best techno-economocial way to consume their final residues – heavy liquid feedstocks or petroleum coke.

Additionally, the refineries are searching for solutions of their emission problems by replacing old furnaces used for the production of power, steam and heat. Gasification is able to serve the refineries with these products, which underlines its excellent integration flexibility.

In such a situation, the existing catalytic reforming as the major source for hydrogen in refineries will not be sufficient anymore to satisfy its growing demand. Consequently, two options for hydrogen production are becoming more important; steam reforming of light hydrocarbons, natural gas or LPG which is used to produce the bulk of hydrogen today or gasification of heavy residues or even petroleum coke.

The special situation of India has to be considered – natural gas resources are limited and a significant part of this is dedicated to the fertilizer industry. Therefore, a number of Indian refineries have already published their intention to proceed or consider Gasification projects for Integrated Gasification Combined Cycle (IGCC), for hydrogen production or in combination for hydrogen and power.

Indian companies have excellent experience with oil and coal gasification dated back to the 1960’s. Oil gasification offers a technology, which has been proven under Indian conditions to provide a reliable source of synthesis gas in industrial service. Over 80% of the Indian plants apply the Shell gasification technology SGP.

Although coal gasification has a good track record around the world, in India it played a minor role compared to oil gasification. This situation is based on the particular characteristics of Indian coal – high ash content (up to 45 %), and the ash containing high amounts of silica and alumina resulting in high meltngs points.

India has proven reserves of 170 billion tons of coal. When compared with reserves of oil (580 million tons) and gas (540 million tons) coal gasification will need to be regarded as a future resource for India. Since most Indian coal has low sulphur contents (approx. 1 %), relatively simple flue gas desulphurization units can be added with low investment cost compared to conventional combustion plants that all have to meet the stringent environmental requirements.
2. Hydrogen production from gaseous and liquid residues

Steam-methane reforming (SMR) has been the conventional route for hydrogen and carbon monoxide production based on feedstocks from natural gas up to naphtha. Several alternative technologies have advantages for a number of applications. These alternatives include:

- Autothermal Reforming (ATR)
- Combined Autothermal Reforming (CAR)
- Gasification.

Any of these technologies has certain advantages or disadvantages for the specific application and local conditions, which have to be considered individually. Figure 1 gives an overview about the processes and typical parameters applied.

<table>
<thead>
<tr>
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<th>Unit</th>
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<th>CAR</th>
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<td>-</td>
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<td>~ 0.6</td>
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</tr>
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<td>500</td>
<td>500</td>
<td>70</td>
<td>150</td>
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</table>

*Figure 1: Synthesis gas production technologies*

The raw gas leaving the different reactors mainly consists of H₂ and CO, small quantities of CO₂ and H₂O, and impurities like CH₄, N₂ and Ar.

A key variable in the design of the plants is the product H₂/CO ratio. For synthesis gas plants, the product H₂/CO ratio varies from 1.0 to 3.0. For hydrogen plants, the ratio is almost infinite. For carbon monoxide plants, this ratio is essentially zero.

Several methods can be applied for the adjustment of the H₂/CO ratio:

- CO₂ recycle
Typically, CO\textsubscript{2} recycle is considered for meeting the desired H\textsubscript{2}/CO ratio, if a large quantity of CO\textsubscript{2} is produced. CO\textsubscript{2} is present in all reactor effluents and is considered as an impurity, which must be eliminated. CO\textsubscript{2} recycle is usually not considered for gasification, because the content of CO\textsubscript{2} in the raw gas is very low. In most designs, CO\textsubscript{2} is removed by absorption in an amine solution. The recycled CO\textsubscript{2} can be converted to CO in the reactor by the reverse water-gas shift reaction.

- **Steam**
  Adding steam to the reactor converts CO to H\textsubscript{2} by the water-gas shift reaction, which increases the H\textsubscript{2}/CO ratio. Gasification normally uses steam as a moderator.

- **Shift conversion**
  The catalytic conversion of CO to H\textsubscript{2} is the only possibility for processes with a naturally very low H\textsubscript{2}/CO ratio to increase the hydrogen yield. Hydrogen production by gasification is exclusively based on shift conversion.

- **Membrane**
  The membrane technique is used for hydrogen purification as well as for lowering the H\textsubscript{2}/CO ratio by removing the hydrogen as a permeate stream. If a small amount of hydrogen has to be extracted from a large synthesis gas stream, a membrane can be a very economic solution. This application is considered for IGCC Power Plants, when a cogeneration of hydrogen is required.

- **Cold Box**
  The Cold Box is often used to separate hydrogen and carbon monoxide into a high-purity CO stream and an H\textsubscript{2}-rich stream. The H\textsubscript{2}-rich stream may undergo further purification (typically in a PSA unit) to yield a high-purity H\textsubscript{2} stream.

Further consideration should be given to the downstream gas cleaning stages in case of the application of feedstocks containing undesired components, such as sulphur and heavy metals. During the refining steps, heavy metals - especially vanadium, iron and nickel - being present in any crude oil, are accumulated in the bottom products. The cheapest feedstocks for gasification units are in fact those residues having the highest metal concentration.

**Gasification** is the only technology to convert even the heaviest “bottom of the barrel” into a wide range of chemical gases including power. In addition to the mentioned gas composition the other impurities H\textsubscript{2}S, NH\textsubscript{3}, COS, HCN and ash have also to be removed from the produced raw gas. Further, a small amount of unconverted carbon is present, ranging from 0.5 to 1.0 %wt on liquid feedstocks or 50 – 200 ppm wt for gaseous feedstocks.
**Shell Gasification Process**

The SGP has a long track record of well performing plants for many years of operation. Historically, the SGP process, initially developed in the 1950’s, was primarily used for fuel oil and bunker C oil as feedstocks. In the 1970’s vacuum (short) residue had become the standard feed. In the 1980’s vacuum residues were even further concentrated by visbreaking and/or C₄/C₅ deasphalting. Thus, over time, the feed became heavier, accompanied by increasing viscosities and higher levels of sulphur and heavy metals. A continuous development effort over the years underpins Shell’s dedication to this technology.

The SGP consists of three principle steps (Figure 2):

![Simplified Process Flow Diagram of a Residual Oil-based SGP Unit for Hydrogen Production](image)

**Gasification**

The non-catalytic partial oxidation of hydrocarbons takes place in the gasifier equipped with a burner (co-annular burner) designed for more efficient gas/liquid mixing and a better flame temperature control.

The oxidant is preheated to minimise oxygen consumption and mixed with steam as moderator prior to feeding to the burner.

The viscosity range of the feedstock has been widely expanded by replacing the pressure atomising burner (blast burner).
Steam shielding ensures a minimum burner life of 8,500 operating hours for heavy residue as the feedstock and an integrated start-up via the main burner is applied. The burner management system includes a sophisticated safeguarding system as well as a sequence logic block allowing the start-up to be fully automated.

- **Syngas Effluent Cooler**
  The raw synthesis gas is leaving the gasification reactor at a temperature of about 1,300 °C containing particles of soot and ash. The recovery of sensible heat in this gas is an integral feature of the SGP process. This takes place in the Syngas Effluent Cooler (SEC), where high pressure steam (e.g. 100 bar) is generated. The raw gas is cooled to about 340 °C. Further cooling occurs for preheating of the Boiler Feed Water, which is used in the SEC. The produced steam is used for preheating of the feedstock and of the oxygen as well as moderator.

  The design of the SEC has been developed specially for these operating conditions and already applied in over 135 installations worldwide.

  Residues originating from all crudes known can be gasified in the SGP without resulting in serious fouling of the SEC coils.

- **Carbon Removal**
  The raw gas produced in any gasification contains a certain amount of free carbon (soot).

  The soot particles are removed together with the ash in a two stage water scrubbing. This consists of a quench pipe and a soot separator followed by a packed column (soot scrubber). In the quench pipe about 95 % of the soot is removed by a direct water spray. The remaining soot is removed in counter current flow in two packed beds.

  After leaving the scrubber the gas has a residual soot content of less than 1 mg/Nm³. The temperature of the gas depends on the final application of the synthesis gas, for hydrogen production about 40 °C.

  The SGP process is not applying a recycling of soot, which leads to a heavy metal build-up in the system.

  The scrubbing water containing soot and heavy metals is routed to a filter press. The main part of the water is recycled as recycle water to the top of the scrubber; excess water is sent to the Sour Water Stripper. This water is free of heavy metals and can be treated in a biotreater. The carbon on the filtercake is burnt off in a multiple hearth furnace and the ash collected (rich in Vanadium and Nickel) is sold to metals reclaiming companies.

  The installation of this Soot Ash Removal Unit (SARU) has operating compared to the formerly used Naphtha Soot Recycling Unit (NSRU). Additionally, the normally accuring
heavy metal enrichment in the gasification reactors based on NSRU is avoided by use of the SARU concept.

**Hydrogen production**

The raw gas leaving the gasification unit contains CO which has to be converted to H₂ by means of a catalyst (CO-Shift). The exothermic reaction leads to a considerable increase of temperature.

Two different alternatives can be chosen regarding syngas use in gas turbines – “sour” or “sweet” shift.

The hydrogen production of Pernis (Figure 3) is a typical line-up for “sweet” shift, where the H₂S removal is executed upstream the catalytic shift reaction.

![Figure 3: Refinery Pernis – Hydrogen Manufacture](image)

For the treating of the raw gas the Rectisol process was chosen. This is a single train unit that integrates sulphur removal with the CO₂ removal downstream the CO-shift. COS and HCN is removed from the syngas by the Rectisol process. If other treating processes are used, a separate COS/HCN hydrolysis (catalytic step) has to be installed. The water (steam)-to-dry gas ratio can be adjusted between 1.8 – 2.4.

In case, that all syngas is used for hydrogen production the H₂S removal and the CO₂ removal is carried out simultaneously in one step after the „sour“ CO-shift. Simultaneously to the CO conversion, COS is hydrolysed to H₂S and CO₂ by a side reaction with water. Similarly, HCN is hydrolysed to NH₃ and CO. The water (vapour)-to-dry gas ratio can be adjusted between 1.3 – 1.8.

The H₂S is converted into elemental sulfur in a Sulfur recovery Unit.
3. Hydrogen production from solids

In the early 70’s Shell and Krupp Koppers (now Krupp Uhde) decided to start the development of a coal gasification process building upon the technology base of pressurised oil gasification. Against the background of the potential applications (power production, chemicals, town gas, synthetic natural gas and transportation fuels) and the environmental requirements, the basic concepts for this process were selected to be:

- Slagging, membrane wall gasifier (high temperatures allowable because of insulation/protection of wall by solid slag layer; inert solid waste),
- Pressurised (compact equipment, high specific throughput, gas turbine application of syngas),
- Entrained flow (compact gasifier),
- Oxygen blown (compact equipment; high gasification efficiencies),
- Multiple, opposed burners (high carbon conversion due to good mixing of coal and blast; high turndown ratio; “easy” scale-up),
- Dry feed of pulverised coal (high efficiency; size/moisture content/caking properties of coal no issue).

Figure 4 gives an overview about the processes and typical parameters applied for SCGP with a standard coal and petroleum coke.

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<td>Methane Slip</td>
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<td>Oxygen/Feed</td>
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</table>

*Figure 4: Typical parameters for SCGP*

**Gasification**

Raw coal or petroleum coke, plus recycled slag fines, is fed to a pulveriser, a conventional roller mill, which grinds the coal to the size suitable for efficient gasification. The gasifier consists of a pressure vessel with a gasification chamber inside. The inner gasifier wall temperature is controlled by circulating water through the membrane wall to generate MP (some 45 barg) steam. Most of the mineral content of the coal leaves the gasification zone in the form of molten slag. The high gasification temperature ensures that the molten slag flows down the membrane wall via the slagtap. This slag layer on the membrane wall protects the membrane wall against severe corrosion and erosion.
Additionally, the high gasification temperature (1400 – 1700 °C) ensures that high carbon conversions are obtained and that no hydrocarbons other than traces of methane are present in the raw syngas. The insulation provided by the slag layer in the gasifier minimises heat losses such that cold gas efficiencies are high and CO₂ levels in the syngas low. Recycling of fly ash can enhance efficiencies for low ash feedstocks. Flux will be added to high ash melting point feedstocks to promote the appropriate slag flow from the gasifier at the preferred operating temperature.

Petroleum coke has a not sufficient ash content. Some ash has to be added to form the protection slag layer on the membrane wall. For reducing the amount of ash added to the petroleum coke the slag will be recycled.

**Syngas Cooling**

The syngas ex gasifier is cooled with recycled syngas in the gas quench at the gasifier outlet to approx. 900 °C before it enters the gas transfer duct and syngas cooler. In the syngas cooler superheated steam is produced. The steam is used as moderator for the gasification process, internal preheating of oxygen and nitrogen and saturation of the syngas. In addition, the remaining steam can be utilized in the refinery for their purposes.

The fly ash is removed from the syngas in a ceramic candle filter. The ash is discharged via lockhopper systems and can, if so desired, be recycled via the coal milling and drying system.

The “solids free” (< 5 mg/Nm³) syngas is partially recycled for quenching.

![Figure 5: Typical SCGP gasifier configuration](image-url)
In 1999 Shell Global Solutions B.V. have been selected for the design of a gasification/hydrogen plant for a grass roots refinery in India. The feedstock for the gasifiers will be petroleum coke, a by-product from the delayed cokers.

The Basic Engineering Design Package (BDEP) for this project was executed by a team consisting of Shell and Krupp Uhde.

The syngas produced will be used for both power generation and hydrogen production. The configuration is similar to that of the Pernis plant.

The sulfur containing syngas from the gasifiers is desulphurised using a COS hydrolysis step followed by H$_2$S absorption using the Shell Sulfinol process.

![Figure 6: Hydrogen production based on petroleum coke with SCGP for India](image)

Part of the sweet syngas is sent to gas turbines, the remainder is used for hydrogen production. The syngas is shifted applying high temperature shift catalyst only. The bulk of the CO$_2$ formed by shift reaction is removed by MDEA solution and final purification is done with a PSA unit.

Because of the high CO content of the syngas a three-stage shift is applied Figure 7). The use of an adiabatic equilibrium reactor would lead to a shift exit temperature well above 530 °C with as consequence a catalyst lifetime of less than 2 years. For this reason the first stage is a kinetically limited reactor.
In order to control the inlet temperatures of the subsequent stages, water quenches are applied. The quench water used is the circulating process condensate which is also used for the saturator column.

The above line-up enables the CO slip to be reduced to below 2 %v.

All three shift stages will be operated at an exit temperature well below 500 °C in order to achieve an extended catalyst lifetime.

The purification of the shifted gas is done in two steps, viz. a bulk CO\textsubscript{2} removal followed by a PSA unit. The PSA unit was selected to meet the customer wish of a hydrogen purity exceeding 99.5 %vol.

The bulk CO\textsubscript{2} removal serves for two purposes, it:
- reduces the size and costs of the PSA unit and
- improves the fuel gas properties of the PSA off gas. Renunciation of the bulk CO\textsubscript{2} removal the offgas would contain approx. 70 %vol. of CO\textsubscript{2}.
4. Outlook

Both Shell Global Solution and Krupp Uhde have an extensive experience in the field of gasification technologies since decades, and a long track record of close co-operation from technology development to successful plant realisation, among which the first IGCC/H₂ complex fully integrated into a refinery (Pernis), as well as the commercialization of the two world’s largest IGCC plants based on solids gasification, being the Buggenum (hard coal) and the Puertollano (petroleum coke) IGCC complexes.

Shell gasification processes have proven their outstanding technical feasibility both in chemical and in power applications. They are very flexible with respect to a variety of different feedstocks and have been successfully scaled up to sizes above 500 t/d (for SGP) and 2000 t/d (for SCGP).

Especially for solid feedstocks, the dry feeding system of SCGP has proven significant advantages in the efficiency of the plant, thus improving the overall feasibility of the investment.

Very heavy residues and coal as well as petroleum coke can be gasified and converted into clean syngas.

Examples of projects given show that especially the combination of power generation and hydrogen production are interesting options. Residual materials are converted into valuable products in an efficient and environmentally attractive way.