New methods upgrade refinery residuals into lighter products

Gasification of bottom-of-the-barrel byproducts can provide operating flexibility due to tighter fuel oil specifications

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Gasification of refinery residue is a method to produce hydrogen, carbon monoxide (CO) or both for chemicals (ammonia, methanol and oxo-alcohols). Recently, gasification is also being used to close the *hydrogen gap* for refineries. This operation is often coupled with further upgrading of refinery bottoms from other unit processes such as solvent deasphalting, coking and visbreaking.

Changes in legislation generate more interest in gasification technology. Existing refineries are challenged to improve the quality of all refinery products while continuously reducing plant emissions. Several case histories demonstrate the potential benefits of incorporating gasification into a complex refinery. The facilities are European sites that applied gasification to solve current refining challenges in an efficient, environmentally friendly and economical way.

CHALLENGES

Approximately 90% of the world's primary energy consumption is derived from fossil fuels. Hydrogen or methane derivates are alternative energy sources but will require considerable time and capital to be fully developed to commercial stage with global applications. Crude oil will be used to meet energy demands, especially for transportation. Presently, refineries must address some known and new challenges:

- Crude oil remains the preferred feedstock
- Possible introduction of bio-crudes
- A changing product slate
- Refinery hydrogen balances
- Cutting deeper into the barrel
- Achieving zero-sulfur products while maintaining throughput
- New processing routes to gasoline
- Adapting processing due to lower heavy fuel oil demand
- Upgrading residue more efficiently.

Additionally, uncertainties bring more operating challenges:

- Advances in combustion engine technology
- Introduction of new technologies, such as fuel cells
- Agendas held and taken by federal and state governments
- Tax and fiscal measures
- Energy, transport and environmental legislation
- Public opinion
- Regional variations.

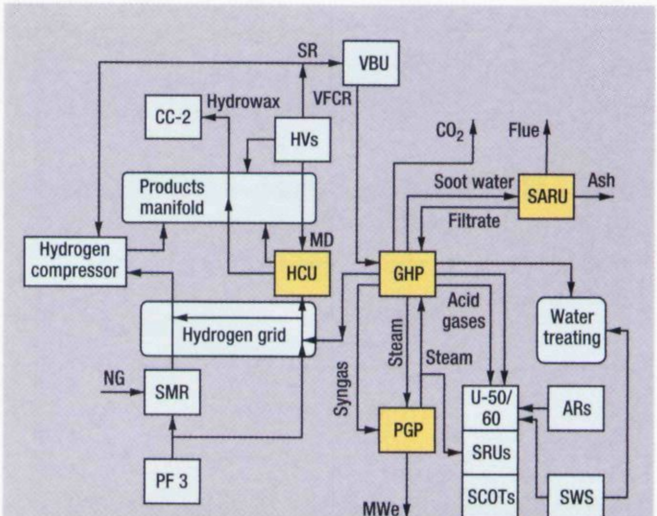

FIG. 1 Process flow scheme in the Pernis Refinery; process includes gasification unit.

Most refineries are being proactive to meet these challenges including environmental issues. For many refineries, their profitability will be challenged, if not threatened, if no action is taken to improve competitiveness, and to meet future product quality and emissions legislation. Long-term strategies should consider power-supply security, quantity and quality needs for the domestic fuel market, and environmental and social benefits.

Recent legislation changes increase pressure on refineries. Globally, diesel and gasoline products must comply with more stringent requirements. European Union (EU) sulfur content directives require an intermediate 50-ppm sulfur (S) level for diesel for 2005 and an ultimate goal of less than 10-ppm S by 2009. These low-sulfur diesel specifications apply to both onroad and offroad diesel.

The sulfur specification for non-marine heavy fuel oil is already 1 wt% in the EU. Between 2005 and 2010, the sulfur content of bunker fuel oils for non-ocean-going applications will be lowered to 1–1.5 wt%. The combination of more stringent sulfur limits for heavy fuel oils for non-marine and non-ocean-going marine applications implies that most of the high-sulfur, fuel-oil market will expire, and the only outlet for high-sulfur fuel oil will be

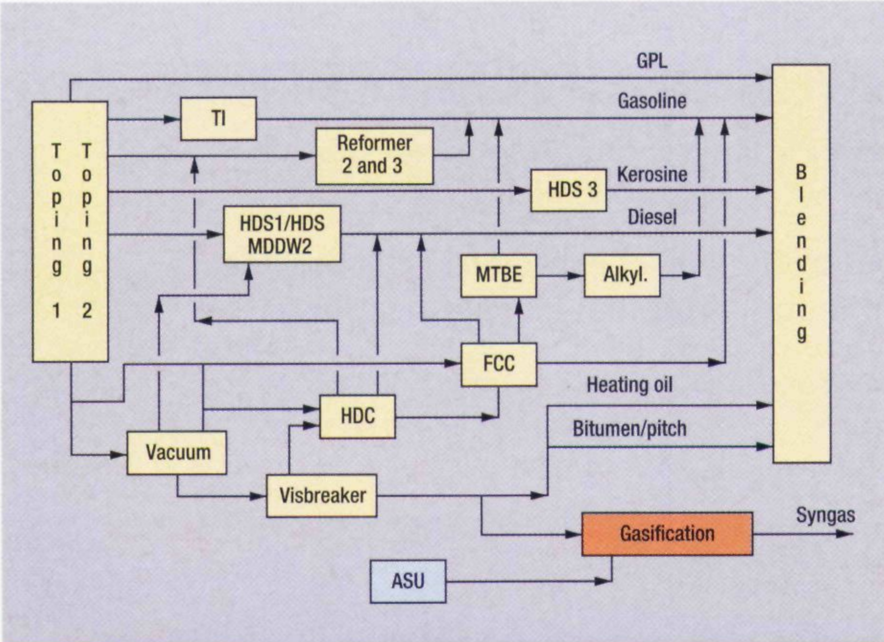

FIG. 2 Integration of a gasification unit into the Sannazzaro Refinery.

TABLE 1. Principle upgrading technologies for liquid residue

Technology	Plus	Minus	Comment
Blending	Simple; cheap	No upgrading No contribution to quality and to environmental	Depending on location of the refinery
Thermal conversion	Cost-effective Distillates good HT feed	Removes 10% (VB) to 40% (DTC) of sulfur	Difficult to store and to blend
Solvent de-asphalting	Maximum recovery of "nonblack" products	Not selective for CCR	Difficult to store and to blend

ocean-going ships. In addition, the refinery must reduce total plant-wide emissions. Using the surplus vacuum residue as a refinery fuel component—after satisfying base oils and bitumen manufacturing requirements—will not be an acceptable solution.

To stay competitive and meet future market demands, the refinery will have to produce lighter, higher-value products that meet EU sulfur-content specifications. Cost-effective disposal of the refinery residue is a major challenge.

Integration. Further upgrading of the bottom-of-the-barrel is one major target to increase light products yields from the refinery. Table 1 summarizes possible upgrading technologies now applied. Both upgrading technologies—thermal conversion or solvent de-asphalting—can yield:

- Very viscous residue
- More heavy metals and sulfur in the residue
- Difficulties in blending
- Difficulties achieving fuel-oil quality.

Gasification of heavy residues can close the gap between blending and disposal problems. Gasification is a versatile process that can convert a variety of hydrocarbon feedstocks such as coal, lignite, oil distillates, residues and natural gas into synthesis gas (syngas)—a mixture of CO and hydrogen.

After gasification, detrimental species (sulfur compounds) can be easily removed. The syngas may be used for its combustion value—particularly as fuel gas for gas turbines in which NO_x emissions are low and can favorably compete against natural gas. Apart from this environmental advantage, syngas has a great value in the petrochemical/chemical industry. Syngas can readily be converted into petrochemical products including ammonia, methanol, oxo-chemicals and, most importantly, hydrogen.

The refinery energy utilization concept will lead subsequently to applying gasification:

- The move to cleaner, more energy-efficient fuels must be accompanied by a drive to reduce energy consumption within the refinery
- Strong reasoning—environmental benefits plus financial payback
- Potential even in the most energy-efficient refineries.

Gasification can provide an integrated solution between the various processing units. Several fundamental aims include:

- Providing cost-effective hydrogen production to meet future products' specification
- Generating power and steam for the refinery usage and export (only balance)
- Producing higher-valued products to improve competitiveness
- Eliminating high-sulfur fuel-oil production
- Developing solutions that can be integrated with the existing refinery complex
- Integrating and implementing the most cost-effective solutions.

Several case histories summarize how gasification technology can be an integral part of a refinery.

Shell Pernis Refinery. The Shell Pernis refinery in The Netherlands was founded in the early 1930s. It is one of the largest refineries of the Royal/Dutch Shell Group, and is a complex site with a capacity of about 18 MMtpy (400,000 bpd). In the late 1980s, a strategic study was started to modernize the refinery for operation well into the 21st century. With aging facilities, tightening environmental requirements and product quality specifications, a step change was required to provide a sustainable future for this refinery.

The age of the existing units also played a role. For example, cat-cracker No. 1 was over 45 years old. Modifying this unit to comply with environmental legislation would be questionable. This resulted in a major refinery rejuvenation project (PER+) in which gasification would play a major role (Fig. 1). The project centered on integrating these processing units:

- World-scale hydrocracking unit—8,000-tpd throughput with a hydrogen consumption of 285 tpd
- 1,650-tpd residue gasification unit to produce hydrogen for the hydrocracker and high-pressure (HP) steam and clean fuel gas for a co-generation power plant

• Co-generation power plant comprising two gas turbine and two steam turbine generators, which consume the excess clean gas from the gasification (not needed for the production of hydrogen) as well as all steam generated from the effluent boilers of the gasification.

Construction began in 1993. The full project was completed by the end of 1997. Construction, (pre)-commissioning and startup was achieved within a tight budget and time frame. No refinery upsets or environmental incidents occurred. With the entire project completed, three key installations are now an important part of the total refinery process.

The new hydrocracker is one of the most important units. Its economic success is dependent upon a steady hydrogen supply. For the hydrogen manufacture, a gasification hydrogen plant (GHP) was designed.

The GHP consists of three parallel gasification trains with a total capacity of 1,650-tpd residue (550-tpd each). Heavy visbreaker residue or a mixture of straight-run vacuum residue and propane asphalt is fed to this unit. The gasification capacity installed is larger than that required for hydrogen production. Thus, excess syngas may be used as a clean fuel for the gas turbines of the co-generation power plant. The capacity of the strings is chosen such that hydrogen for the hydrocracker can be produced by two gasification strings—the maximum is 285 tpd.

The raw syngas is treated to remove acid gases and sulfur compounds. A one-string unit integrates sulfur removal with the CO_2 removal downstream the CO-shift. Subsequently, the CO-level is reduced to 1 vol% (dry) in two stages (HTS and LTS).

The majority of the CO_2 (about 3,000 tpd) is released to atmosphere. To minimize methanol emissions (150 mg/m^3 is a limit) before venting, the CO_2 is water-washed. Residual carbon oxides are converted in a catalytic methanation reaction yielding hydrogen well over 98 vol% purity at a pressure of about 47 bar.

AGIP Sannazzaro Refinery. Due to progressive reduction of the heavy residue market, Italian refineries had to reduce their production or find new applications. In response, the Sannazzaro refinery studied several alternatives:

• New coking unit
• Selling of transportation fuel oil as bunker fuel
• Gasification of residue to produce syngas for gas turbine and valuable hydrogen for the refinery.

The last option was considered as part of integrating with a new 1,050-MWe natural gas power plant. The cost/benefit analysis for the different options identified the gasification option. The main reasons supporting this route (Fig. 2) are:

• A definitive and profitable solution to convert the bottom of the barrel—The refinery could convert fuel oil production (about 5% of total present refinery production) to syngas production.

• A consolidated technological solution—Well-proven gasification technology was considered.

• A lower environmental impact compared with other possibilities—Gasification minimizes SO_2 emission via H_2S removal system. NO_x emissions are reduced via standard emission control technique of the gas turbines.

For the gasification plant configuration concerns, several special features were chosen:

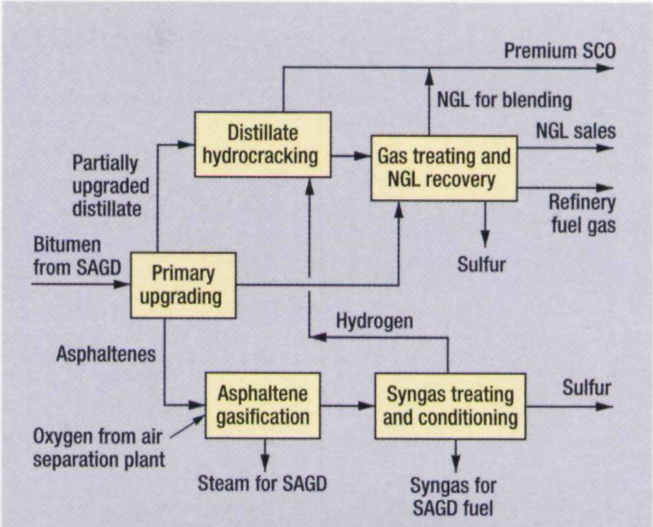

FIG. 3 Process flow diagram of the Opti Canada upgrader with a gasification unit.

• Syngas heat recovery with HP steam production over quench technology to increase efficiency
• Syngas effluent cooler with internal superheater to avoid installing a new furnace to superheat the HP steam
• Soot ash removal unit (SARU) to minimize solid waste production, creating a vanadium concentrate that is easier to handle
• Hydrogen recovery unit to obtain a valuable utility to support hydrogen needs for desulfurization processes
• Chemical H_2S removal, vs. physical, sufficient to guarantee purity of the syngas
• Carbon dioxide is available for sale
• Installing a metal-carbonyls removal unit to avoid forming metal deposit in the gas turbine burners.

Syngas will be produced via gasification of visbroken vacuum tar in two 600-tpd gasifiers, i.e., slightly larger than those already operating in the Shell refinery in Pernis. Hot syngas is cooled, producing superheated steam, and scrubbed with water. Before the syngas is exported to the power station, it is desulfurized; metal carbonyls are removed; and some hydrogen is extracted for refinery usage. Soot produced during gasification is washed out, and resulting water is sent to a filtration unit to separate the soot from water as a cake. The filter cake is sent to a multiple-hearth furnace in which carbon is burned off. In the SARU, a vanadium-rich ash is produced that can be sold. The main part of the filtrate is recycled to the gasification section, and excess is stripped in a wastewater stripper and sent to disposal. The process condensate from the acid-gas treating facilities is treated in the wastewater stripper.

Opti Canada Upgrader Project. The first phase of the Long Lake project comprises 72,000 bpsd of steam-assisted gravity drainage (SAGD) production and onsite upgrading—an in situ thermal recovery process to mine oil-sands deposits. The primary upgrading at Long Lake is accomplished by using a combined distillation, solvent deasphalting and thermal-cracking process. This method converts the raw bitumen into a bottomless, sour synthetic crude and a stream of heavy, liquid asphaltenes.

The sour synthetic crude product is fed to a hydrocracker, where it is further upgraded to a sweet synthetic crude with

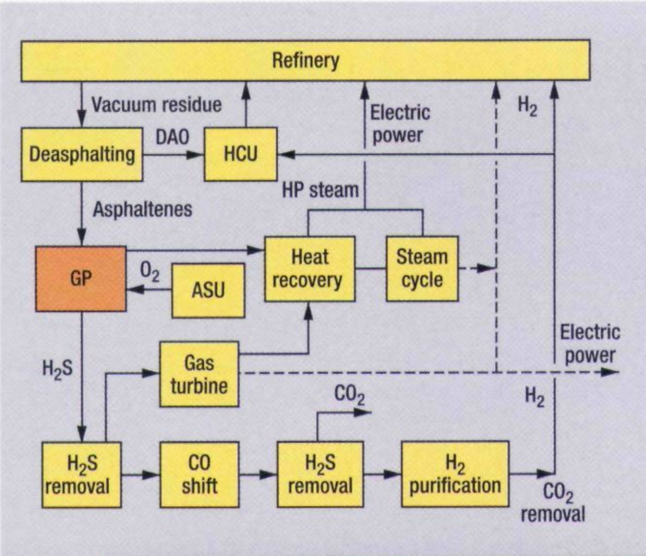

FIG. 4 Flow diagram of the Gdańska refining complex that includes a gasification unit.

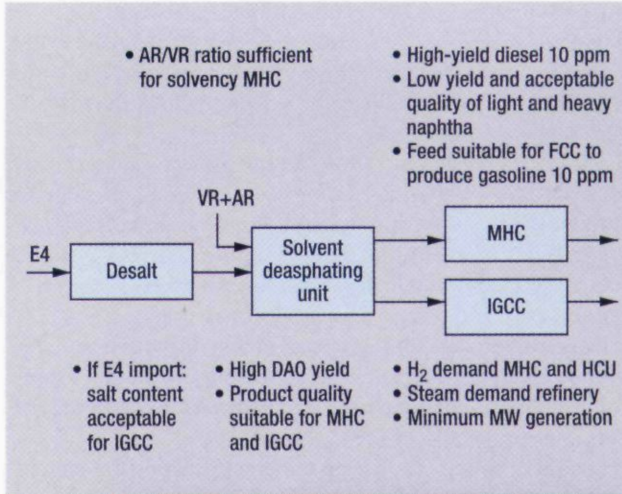

FIG. 5 Simplified block flow diagram of the new upgrading units at the Gdańska refining complex.

premium properties. The asphaltenes from the syncrude unit are fed as a liquid to the gasification system.

The Long Lake Project uses four gasifiers with a capacity of 1,033 tpd (each), each with dedicated syngas coolers generating 77 bar steam (Fig. 3). The steam from the syngas coolers is integrated in the upgrader system to provide process steam to other operating units, along with other fired and non-fired steam sources.

Cooled syngas from the gasifiers is combined and treated in a single acid-gas syngas treating system. After treatment, most of the syngas is directed to a pressure swing adsorption (PSA) unit to recover hydrogen. Sufficient hydrogen in the syngas can meet the upgrader's hydrogen requirements; no CO-shift reactor is needed. The PSA unit can attain the required hydrogen recovery level with a relatively high tail-gas pressure. The tail gas from the PSA can flow directly to users (primarily steam generators) without compression. No CO-shift is used, and due to the low CO_2 generation rate from the gasifiers, the tail gas has a low CO_2 concentration and a heating value that is approximately the same as raw syngas.

Grupa Lotos Gdańska Refinery. Grupa Lotos SA (LOTOS), formerly Rafineria Gdańska SA, is the second-largest refinery in Poland. This coastal hydrocracking and lube oil refinery has an annual processing capacity of 4.5 million tons (MMton) of crude oil. In May 2005, the capacity of the refinery was increased to 6 MMton. The existing refinery facilities include a vacuum-gasoil hydrocracker and conventional base oils manufacturing complex together with traditional primary distillation and treating facilities. The main refined products are gasoline, jet fuel, diesel, lube oils, marine oil and modified bitumen.

Fig. 4 shows the integration of the gasification unit into the existing refinery complex. The LOTOS project centers on integrating these new units. Fig. 5 details the process flow scheme with the gasification unit:

• Deasphalting unit to separate asphaltenes from the vacuum/atmospheric residue feed

• World-scale hydrocracker to process deasphalted oils (DAO)—primarily to low-sulfur diesel and hydrowax (desulfurized oil)

• Gasification unit to produce hydrogen for the hydrocracker and syngas as a source of clean fuel for the power plant as an integrated gasification combined cycle (IGCC)

• Cogeneration power plant with two gas turbines and two steam turbine generators that will use excess syngas and steam generated by the waste-heat boilers of the gasification process.

The deasphalting unit is based on residual oil supercritical extraction technology, which separates valuable lighter products from the heavy residue using the differing solubilities of the components. A blend of vacuum and atmospheric residue is the feedstock for the unit. At a nominal throughput of 330 tph, the deasphalting unit will produce about 260 tph of DAO for the hydrocracking unit and 68 tph of asphaltene for the gasification section. The deasphalting unit will allow flexibility to process various feedstocks from different crude oils.

In the hydrocracker, DAO is demetallized and converted to lower-molecular-weight products such as naphtha, kerosine, diesel and hydrowax. The unit will have a nominal throughput of 260 tph of DAO using 6.5 tph hydrogen from the gasification section with a catalyst cycle length of one year.

The diesel product will meet 10-ppm S specifications. Separate kerosine and diesel product fractions will allow flexible operation including different split for seasonal products (for example, winter properties) or special, temporary requirements. The desulfurized and demetallized hydrowax can be sold as a fluid-catalytic cracking feedstock for 10-ppm S gasoline without further post-treatment or as a low-sulfur component for a fuel-oil pool or as gas-turbine fuel.

The concept of the gasification unit is similar to the Shell Pernis Refinery: Based on three gasifiers, with a total capacity of 1,632 tpd (each 544 tpd), acid-gas syngas treating unit (H_2S/CO_2 removal), CO-shift and hydrogen purification.

Fujian Refinery Ethylene Project. The Fujian Refinery Ethylene Project will expand the existing refinery in Fujian Province from 80,000 bpd (4 MMtpy) to 240,000 bpd (12 MMtpy) with significant product upgrading capability. The upgraded refinery will be designed to process sour Arabian crude. In addition, this project involves constructing a new 800,000-tpy ethylene steam cracker, polyethylene and polypropylene units, and a new 700,000-tpy paraxylene unit.

In this project, a gasification unit produces synthesis gas from de-asphalted rock. The synthesis gas will be used for the generation of power and hydrogen via CO-shift, acid-gas removal unit and PSA unit. Generated hydrogen is used for closing the processing gap after the capacity increase.

The asphaltene stream from the deasphalting unit contains aromatic compounds and high levels of sulfur and metals. The stream will be fed to two parallel-operating gasification trains with a total input capacity of 1,200 tpd (each). The capacity of each train is such that one train can produce the required processing hydrogen supply. An additional third gasification train allows maintenance during the four-year maintenance and inspection cycle.

The raw syngas leaving the gasification unit is split into a stream to CO-shift and a stream going to the acid-gas removal unit, where it is desulfurized as feed for the gas turbines. H_2S and CO_2 are removed. The hydrogen is purified via a PSA unit.

The core technology is the gasifier and specially designed syngas-effluent cooler. The gasifier is a refractory-lined, low-alloy steel vessel. In the gasifier, the reactants are fed to a single, top-mounted, co-annular burner. This burner provides proper atomization of the highly viscous fuel and intimate mixing with the oxygen. The oxygen necessary for the gasification process is delivered from an air separation unit and is admixed with steam, which serves as moderator. The product of the partial oxidation at 1,300°C and 65 bar is a raw syngas containing particles of soot and ash. The raw gas is cooled to 400°C in the syngas effluent cooler, and the heat recovered is used to produce very HP steam at about 125 bar. This very HP steam generation is a special requirement to integrate the gasification unit into the petrochemical complex, especially the ethylene cracker.

Outlook—fit for 2010 and beyond. Gasification technology has been demonstrated and proven to add flexibility for refinery complexes under different requirements:

- Solvent de-asphalting
- Deeper conversion.

Both upgrading technologies yield a more viscous residue with a higher ash and sulfur content. Integrated with other refinery units, the gasifiers are often an optimum solution. Combined with deep-thermal cracking or solvent de-asphalting, gasification converts the residue into low-sulfur finished products and feedstock for the low-sulfur gasoline market. By upgrading residue, heavy fuel oils are no longer manufactured. As a proven technology, gasification can convert the refinery's "bottom-of-the-barrel" products into valuable products. Gasifiers can be optimal integrated into power blocks (IGCC) and petrochemical complexes. The steam generated in the syngas effluent cooler can be adjusted according to the final steam quality requirements; steam between 75 bar and 125 bar can be generated. Additionally, steam superheating is applied to generate steam and power efficiently.

By implementing the world-scale residue-upgrading projects combined with gasification technology, the key strategic drivers of both the refinery and the community will be satisfied:

- Enhance financial performance
- Eliminate high-sulfur fuel oil exports
- Replace obsolete utility facilities
- Meet future product specifications
- Improve the environmental performance of the refinery (reduce total refinery emissions)
- Provide cost-effective H_2 production based on converting residue
- Produce power for refinery use and export (balance)
- Increase feedstock flexibility—chance to use lower-cost crudes
- Secure or even expand employment and business opportunities in the region. **HP**

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