FLEXICOKING[™] Technology Resid Conversion Solution for Refinery Energy Optimization as Demonstrated in the Hellenic Petroleum Elefsina Upgrade Project

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FLEXICOKING technology is a highly differentiated unique resid upgrading process resulting in significantly lower environmental emissions than other conventional coking technologies, and production of a clean burning fuel gas available for refinery energy optimization. These environmental and energy utilization advantages result in an improved economic resid conversion solution for processing difficult heavy feedstocks.

This paper focuses on two main themes...

- 1. An overview of the technology highlighting over 40+ years of process performance with a focus on flexigas utilization.
- The real world benefits as well as project implementation and operational considerations associated with the HELPE Elefsina Refinery Upgrade project including FLEXICOKING technology and services.

FLEXICOKING technology is a commercially proven fluid bed resid upgrading process, designed for thermal coking all types of residue feeds with minimal coke production; as low as 1 percent of feed is converted to coke product. The unique design eliminates the open coke pits and associated particulate emissions with enclosed coke transfers. Also, there is no high sulfur petcoke production to market and no coke drum deheadings associated with delayed coking. FLEXICOKING technology gasifies the majority of the produced coke with steam and air to produce a fuel gas referred to as **flexigas**. During gasification, sulfur in the coke is converted into H₂S which is removed via amine absorption included within the battery limit of the unit. The clean flexigas supplements the refinery fuel gas and can be used in process heaters, utility boilers and power generation. Thus, FLEXICOKING provides an environmentally friendly technology solution for upgrading all types of refinery residual streams to liquid products and converting coke to clean burning fuel for optimizing the refinery energy integration.

This article provides a comprehensive overview of ExxonMobil's technology and utilization of flexigas for refinery energy requirements. This article will also discuss the application of the technology in the Hellenic Petroleum (HELPE) Elefsina Refinery in its 2012 Refinery Upgrade Project and subsequent energy balance optimizations facilitated by the project.

EXXONMOBIL FLEXICOKING™ TECHNOLOGY OVERVIEW

Resid Conversion Technology Alternatives

Resid or residuum materials are high boiling hydrocarbons that are not suitable for transportation fuels or lubes unless they can be converted to lighter, more hydrogen rich hydrocarbon types. There are two basic approaches to processing these feedstocks to more valuable lighter products. These are referred to as hydrogen addition or carbon rejection.

Hydrogen addition processes usually operate at high pressure and depend upon catalysis and hydrogen gas to achieve the desired reactions, which simultaneously crack and hydrogenate the large residuum molecules. These heavy feedstocks generally cause catalyst deactivation at a significant rate due to the presence of hetero atoms and metals, requiring high fresh catalyst makeup rates. Hydrogenation is indiscriminate and the resultant high hydrogen demand can be expensive at locations where hydrogen is costly. These processes also produce a bottoms stream of very low quality that is difficult to dispose of in a cost-effective manner.

Carbon rejection processes generally refer to thermal coking processes which operate at low pressure (less than 0.4 MPa-g/60psig) and utilize thermal cracking reactions to achieve the desired conversion of the high boiling molecules. Thermal cracking reactions refer to several types of reactions including cracking, condensation, polymerization and isomerization. This chemistry results in a redistribution of hydrogen in the feed to yield lighter liquid products with higher hydrogen-carbon ratios and a byproduct of solid coke with low hydrogen-carbon ratio. Typical commercial coking processes include delayed coking, fluid coking, and ExxonMobil's unique **FLEXICOKING** technology. Solvent de-asphalting is an alternative carbon rejection process which separates carbon rich asphaltenes by solvent extraction from a more hydrogen rich de-asphalted oil that can be processed in conventional FCCs or hydrocrackers. The asphaltene pitch or "rock" is typically disposed of in fuel oil blending or a coking process.

Process Description

FLEXICOKING technology utilizes a low pressure process that integrates fluid bed thermal coking with a fluid bed steam and air coke gasification. The feed is converted to high value full-range liquid products, conventional fuel gas and a CO / H₂ based fuel gas referred to as flexigas. Process heat for the thermal conversion and gasification steps is provided by partial oxidation of carbonaceous coke formed in the coking reactor. Most of the coke is gasified and the resulting gas is desulfurized using the proprietary FLEXSORB[™] technology. The significant volume of clean flexigas can be used in refinery fired equipment for power generation or for other energy needs. The Unit at HELPE Elefsina Refinery utilizing FLEXICOKING technology is shown in Figure 1.



Figure 1. Unit at Hellenic Petroleum Elefsina Refinery

PROCESS DESCRIPTION

The process consists of three main vessels: coking reactor, coke gasifier, and reaction heater. The typical process flow and energy balance for the FLEXICOKING[®] technology is shown in Figure 2.

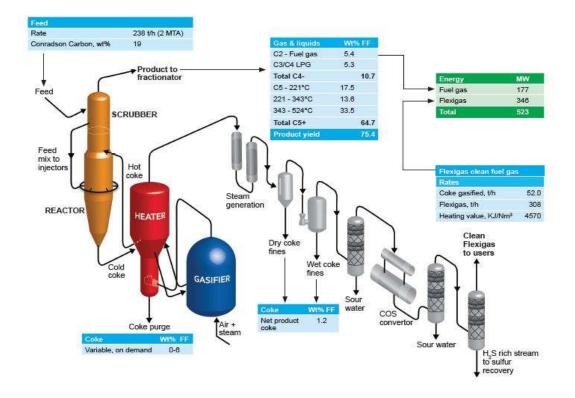


Figure 2. Products and Energy Balance

The vacuum residue feed enters a scrubber section located at the top of the coking reactor for direct contact heat exchange with the reactor overhead product vapors. The higher-boiling point hydrocarbons (~975°F+/525°C+) present in the reactor product vapors condense in the scrubber and return to the reactor in a mixture with the fresh feed. The feed is thermally cracked in the reactor fluidized coke bed to a full range of gas and liquid products and coke.

Lighter overhead product vapors from the reactor/scrubber go to conventional fractionation and light-ends recovery where the liquid products and LPG are produced.

Coke inventory in the reactor and heater is maintained by circulating coke from the reactor to the heater via the cold coke transfer line. In the heater, the coke is heated by contact with the gasifier products and circulated back to the reactor via the hot coke transfer line to supply the process heat that sustains the thermal cracking reaction. The excess coke in the heater is transferred to the gasifier where it reacts with air and steam to produce CO / H_2 rich syngas called flexigas. The gasifier products, consisting of a mixture of flexigas and unconsumed metals rich coke, return to the heater to heat up the circulating coke.

Flexigas exits the heater vessel and is fed to steam generators before going to dry and wet particulate removal and then to H_2S removal in the integrated FLEXSORBTM technology amine absorption process. FLEXSORBTM technology is designed for selective removal of H_2S in the presence of CO and CO₂ and utilizes a proprietary severely sterically hindered amine. This allows the FLEXSORBTM technology solvent to achieve high H_2S cleanup selectively at low solvent circulation rates. The flexigas product contains less than 10 vppm H_2S and is ready for use as fuel in fired process heaters and/or boilers for steam and power generation.

FLEXIGAS BENFITS AND UTILIZATION

Integration of coke gasification into the fluid bed coking process has multiple benefits:

Reduced Coke Handling and By-Product Disposition: Minimal coke production reduces the requirement for containing and managing sales or disposal of large quantities of high sulfur coke produced in the traditional delayed coking processes or residual bottoms streams produced in hydrogenation processes.

Low Particulate Emissions: Processing and handling the coke in a continuous closed system minimizes particulate emissions vs typical coking operations.



Figure 3. Silo utilizing the FLEXICOKING technology

Plot Space: Conversion of the majority of the coke within the unit reduces the plot area and refinery infrastructure required to manage coke movement and shipping.

Operations Flexibility: Coke gasification can be optimized to satisfy operational requirements such as changes in feed qualities and variations in refinery fuel demand. This flexibility is a critical enabler for a site-wide zero flaring strategy.

Low Capex: The low operating temperatures and pressures of the technology allow for the use of low cost carbon steel with refractory vs. other gasification alternatives. Also, the management of coke transfers in a fluidized system reduce space and material handling costs. Also, simultaneous gasification and desulfurization reduces costs associated with desulfurization of the resid feed or coke.

Environmental Benefits: The flexigas produced in the gasifier burns very clean with ultra-low production of Sulfur Oxides (SO_x) or Nitrogen Oxides (NO_x) when consumed in fired heaters or boilers. The lower NO_x is the result of the nitrogen content of the flexigas which lowers the adiabatic flame temperature during combustion resulting in significantly lower NO_x production than natural gas or conventional refinery fuel gas. The sulfur contained in coke is converted to H_2S in the gasification reactions. The level of H_2S in the flexigas is controlled to a low level (<10 vppm) through the removal by amine absorption within the unit battery limits.

Energy Production: Production of flexigas from coke provides additional energy for use in the refinery and/or to integrate with neighboring facilities such as power plants, steel manufacturing, cement plants and others for energy production/gas sales.

Economic Benefits: Depending on local market conditions, flexigas can substantially reduce refinery energy cost versus fuel oil, natural gas, or purchased power.

Flexigas Utilization Considerations

Flexigas is used in boilers and most types of fired heaters and the capability of existing equipment to fire flexigas has been proven for over 40+ years.

Flexigas is typically fired in combination with a small percentage of refinery fuel gas or natural gas to maintain a dual fuel strategy. Grassroots flexigas fired equipment is designed for 85 percent flexigas gas firing (heat release basis) and 15 percent refinery fuel gas (RFG) firing. This flexibility is required since RFG production rate and quality from various refinery units will vary with feed rate and feed composition. Though flexigas has a lower heating value and lower flame temperature, it burns readily and is capable of smooth and self-sustained combustion.

Separate fuel distribution systems are required for flexigas and refinery fuel gas due primarily to the large volume of flexigas and the low supply pressure of approximately 100 kPa-g (15 psig). Segregated fuel gas headers also allows independent flexigas control at individual boilers and process furnaces.

Flexigas properties are within the range of commercially proven fuels. Typical composition of flexigas is shown below in Figure 4.

Comp, vol %	Typical Flexigas	Blast Furnace Gas	Refinery Fuel Gas	Natural Gas
C1-C4	1.4	0.1	73	100
H2	15.7	5	20	
CO	23.7	22	0	
CO2	6.7	18.5	0	Trace
N2	49.7	54.4	5 (Inerts)	Trace
H2O	2.8	0	2	
LHV,BTU/SCF	130	93	1000	917
LHV, MJ/Nm3	5.1	3.5	39.2	36.1

Figure 4. Typical Composition of Flexigas and Other Fuels

Flexigas has a Lower Heating Value (LHV) of about 120 - 130 Btu/SCF (\sim 5.1 MJ/Nm³) compared to natural gas at 900 to 950 Btu/SCF (\sim 36.1 MJ/Nm³), but it is higher than some fuels such as blast furnace gas, which is used in other industries. The relatively low heating value of flexigas is due to the nitrogen content associated with use of air in the gasifier. This level of inerts results in the adiabatic flame temperature of flexigas being 500 to 600 °F (260 to 315 °C) lower than that of a typical refinery fuel gas. This low flame temperature results in lower NO $_{\rm x}$ production than natural gas or refinery fuel gas. Despite the low flame temperature, flexigas is a very stable fuel to burn. This is primarily due to the hydrogen and CO content of the fuel, both components having very wide flammability limits. Flexigas is characterized by stable heating value and low NOx and SOx production during the combustion. Unlike refinery fuel gas, flexigas has a constant heating value, which improves firing stability in furnaces and boilers.

Flexigas Firing Impact on Heat Transfer

The lower adiabatic flame temperature influences the heat transfer split between the radiant section, or firebox zone, and the convection section in fired heaters and boilers. With a lower flame temperature, less heat is transferred in the radiant zone and radiant/convective split shifts toward the convection zone. At a typical radiant zone exit temperature of 1800 °F (980 °C), 42 percent of the total heat available from combustion of flexigas will be transferred to the radiant section heat transfer surface.

For a typical fired heater or boiler with both radiant and convective heat transfer sections and the same process in both sections, the shift in duty can be easily handled during the design of grassroots equipment without a significant effect on overall size of the unit, with attention to services such as embedded superheaters. The convection zone is generally larger when compared with a typical fired heater or boiler fired on refinery fuel gas. The radiant zone size will depend upon whether full load capability is required when firing 100 percent RFG. Firing rates are only marginally higher with flexigas, therefore, the same number of burners with the appropriate size adjustment should handle the duty. For equipment where the primary process is only heated in the radiant section, the reduced radiant efficiency when firing a high level of flexigas results in a significantly increased firing rate and greater quantity of flue gas to the convection section. The convection section and services, such as steam generation, need to be sized to take this into account.

Flexigas Firing Experience and Burners

Many different grassroots and revamped fired heater types in a variety of refinery services are firing flexigas. These services include atmospheric and vacuum distillation units, catalytic naphtha reforming, various fired reboilers and hydrogen plant steam reformers. Flexigas is fired in refinery and power plant boilers as well as Heat Recovery Steam Generators (HRSG) in power/steam cogeneration plants.

SITE	Atmospheric Distl	Vacuum Distl	Hydrocracker	Steam Boiler	CO-GEN Plant	H2 Plant - Steam Reformer	Waste Heat Boiler	Steam Superheater	55	Naphtha Reformer	Hydrotreater	Delayed Coker
ExxonMobil	~	~		~		v		~		~		
ExxonMobil	~	~		v			~	~		v		
Licensee 1	~	v		~	~			v				
Licensee 2	~	v	~		~	~						
Licensee 3	~	v	~	~		~		v	v	~	v	~
Licensee 4	_	v		~				v	J			

Figure 5. Current applications of flexigas

In many cases, existing fired heaters have been revamped with modest modifications to handle flexigas firing up to approximately 65 percent of the total heat release with the balance of the fired duty coming from refinery fuel gas. In these cases modifications can be limited to installing new multi-fuel burners, flexigas piping and minor convection coil changes. The most common fired heater services that have been revamped to maximize flexigas consumption are the large fuel consumers such as atmospheric distillation unit heaters, vacuum distillation unit heaters and catalytic naphtha reformer heaters. Of course, no one solution fits all cases, and depends upon the specifics at each refinery.

Flexigas Burners available in a wide range of models

Several vendors have the capability to provide the burners needed to combust flexigas for a project. A range of commercially proven burner types and models are available for firing flexigas in both new and existing fired heaters, boilers and HRSGs. Flexigas is being used in a variety of commercially available burners including raw gas, premix, natural draft and forced draft models. Both tangentially fired and wall fired refinery utility boilers are utilizing flexigas. Duct burners in auxiliary fired Heat Recovery Steam Generators (HRSGs) typically found in cogeneration plants are also being fired on flexigas.

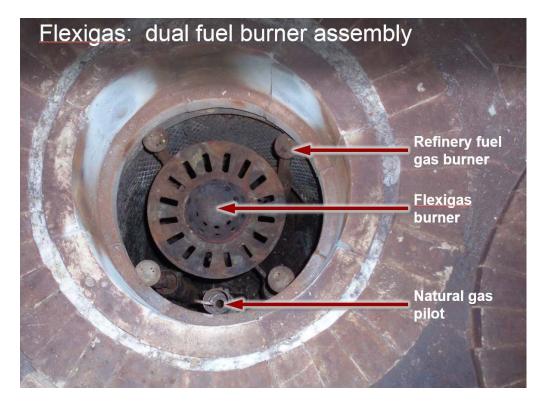


Figure 6. Flexigas: dual fuel burner assembly

ELEFSINA REFINERY UPGRADE - CASE STUDY

The following is a summary outlining key activities and considerations for Hellenic Petroleum's Elefsina Refinery Upgrade Project. The FLEXICOKINGTM resid conversion technology was selected and the project was successfully started in 2012.

- A. Refinery Profitability Study
- B. Factors for choosing FLEXICOKING technology
- C. Refinery Upgrade Implementation Plan
- D. Refinery Fuel System Design Philosophy

A. Refinery Profitability Study

Hellenic Petroleum (HELPE) is an energy sector company located in Greece, with activities spanning the energy value chain ranging from the core business of refining and oil product retail to upstream exploration, natural gas and electricity production.

One of four refining sites owned by Hellenic Petroleum, the Elefsina Refinery is located near Athens and started operations in 1972 as a hydroskimming refinery with a 100 KBD capacity. In 1988, a Hydro-desulfurization unit of 17.5 KBD capacity was added to comply with automotive diesel specifications. In 2004, HELPE commissioned a refinery profitability study with focus to upgrade refinery product slate to improve competitiveness by upgrading the fuel oil to more valuable products.

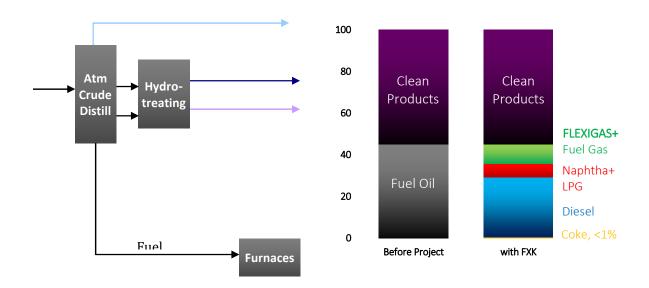


Figure 7. Original Elefsina Refinery Configuration

The Elefsina Refinery profitability study identified the optimum run plan configuration, which included a grass roots crude vacuum distillation unit, hydrocracking and the resid upgrading unit. The plan was to convert 2.2 million tons annually of low value high sulfur fuel oil into 1.4 million tons of high value Euro-V diesel, 0.4 million tons of Naphtha and clean fuel gas. The unit incorporated FLEXICOKING™ technology producing clean fuel gas allowing optimal complex energy integration while minimizing SO_x, NO_x, and particulate emissions and their impact on the local environment.

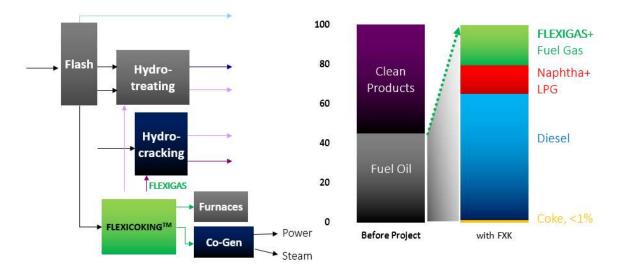


Figure 8. Elefsina Refinery Configuration with FLEXICOKING technology



Figure 9. Elefsina Refinery Complex with FLEXICOKING technology

Various technologies for processing heavy residue were evaluated with FLEXICOKING technology becoming the preferred choice because of its unique advantages for the Refinery:

- **Significantly less capital cost** compared to hydrogen addition technologies. Elimination of the environmental issues associated with disposal of the bottoms stream produced by hydrogen addition technologies.
- **Near elimination of coke byproduct** to as low as 1 wt percent of the feed rate (compared up to 30 percent for delayed coking). Low coke production minimized logistical and coke disposition concerns. The minimal produced coke from the gasifier is low in sulfur and is a well-accepted fuel for cement and power plants.
- Conversion of most of the residuum to high value liquids in roughly equivalent yields of conventional coking. See representative yields in Figure 10.
- Significantly reduced stack emissions and improved refinery energy economics associated with utilization of flexigas to back out imported low sulfur fuel oil (LSFO). See Figure 11 for the improvements in environmental performance of the Elefsina refinery after incorporating a unit containing FLEXICOKING technology.

• **Lower particulate emissions** than conventional coke material handling associated with typical delayed coking operations.

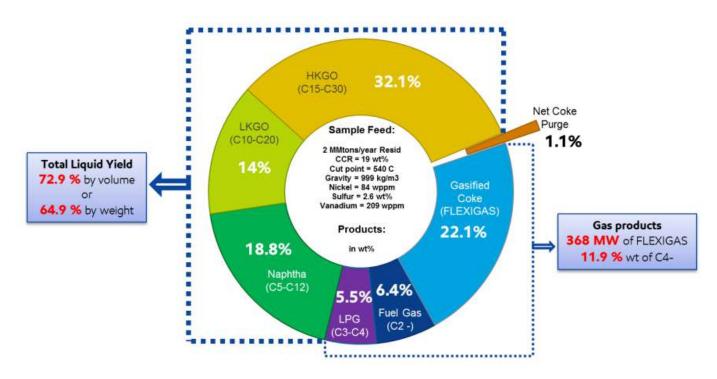


Figure 10. Representative Product Yield utilizing FLEXICOKING™ technology

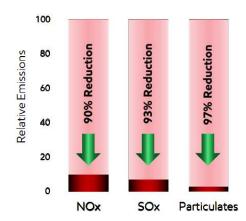


Figure 11. FLEXICOKING technology enabled Major Improvement in Environmental Performance

C. Refinery Upgrade Implementation Plan

Prior to the upgrade project, the refinery consisted of two crude distillation units, a hydrodesulphurization complex, and limited utilities, and was surrounded by a significant tank farm

and a high capacity jetty. The target of eliminating fuel oil production was to be achieved through the following facilities:



Figure 12. FLEXICOKING[™] technology implemented at Hellenic plant

- ✓ Bottom of the barrel section including a new vacuum distillation unit and FLEXICOKING technology;
- ✓ Products upgrading section including a new high severity hydrocracker integrated with a hydrotreater and hydrogen production (steam reformer);
- ✓ Supporting process units section including amine, sour water and sulfur recovery; and,
- ✓ Utilities Section including HP steam production, Steam Turbine Generators, BFW treatment, cooling water, fuel gas system, flare system.

D. Refinery Fuel System Design Philosophy

The unit containing FLEXICOKING technology was integrated into the upgraded refinery configuration as one of the three branches of the refinery fuel system:

- 1. Refinery fuel gas system;
- 2. Flexigas system; and,
- 3. Imported low sulfur fuel oil distribution grid

The refinery fuel gas system, which is fed by fuel gas from process units, is supplemented by liquefied petroleum gas vaporization and natural gas import if required. Flexigas is distributed via a separate flexigas system. Low sulfur fuel oil supplements the fuel balance in normal operation and is a reliable external fuel source in case of cold start up or abnormal operation.

The upgraded refinery fuel philosophy targeted zero flaring with full utilization of refinery fuel gas, minimum fuel oil imports and variable coke gasifier intensity adjusted for zero flaring while meeting the refinery fuel demand.

Prior to the refinery upgrade project, 90 percent of the firing duty was supplied by fuel oil. After completion of the refinery upgrade project, the fuel system philosophy called for minimizing fuel oil firing, substituting it with clean burning gaseous fuels. The driving force behind minimization of the fuel oil firing were environmental factors – fuel oil produces more particulates, SOx and NOx emissions as compared to gaseous fuels and in particular when compared to flexigas. After project startup, the vacuum distillation unit furnace and boilers required 20 percent of the duty to be supplied by fuel oil firing due to the limited capacity of the back-up natural gas supply system. After completing post startup efficiency improvement projects, the current fuel oil demand of the Elefsina refinery is 9 percent of the total energy balance as shown in Figure 13.

Currently, no fuel oil is produced at the Elefsina Refinery, as the gas oil from the vacuum distillation unit is processed in the hydrocracker and the vacuum resid is processed in the unit containing FLEXICOKINGTM technology. The fuel oil required to balance refinery energy demand is imported from the nearby Aspropyrgos Refinery.

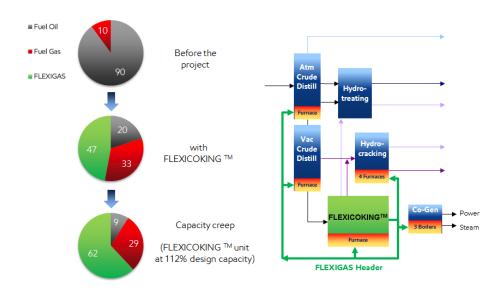


Figure 13. Evolution of refinery fuel gas system after unit containing FLEXICOKING $^{\text{TM}}$ technology is integrated with subsequent expansion to maximize flexigas utilization within the refinery

REFINERY CAPACITY EXPANSION FIVE YEARS AFTER THE UPGRADE PROJECT

After the upgraded Elefsina Refinery successfully started up in 2012, several improvement projects aimed at gradual capacity increase were implemented starting in 2012 to the present. See Figure 12 post-upgrade project capacity creep and optimization.

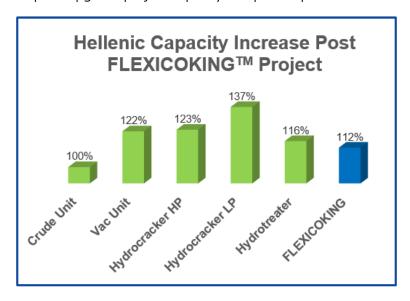


Figure 14. Post-upgrade project capacity creep and optimization

Since the upgrade project, the refinery external energy demand changed as the result of the capacity increase of the Elefsina Complex, which was mainly driven by resid upgrading and hydrocracking unit capacity enhancements, offset by the implementation of energy optimization projects. Reliable operation of the unit incorporating FLEXICOKINGTM technology has permitted the day-to-day optimization of the fuel balance by backing out imported fuel oil with more economic and environmentally attractive flexigas, while still ensuring system reliability and stability against abnormal operation.

The amount of flexigas production was intentionally increased through higher unit feed rate, heavier feedstock and higher gasification rate (lower net coke production). The Refinery has seen a significant economic incentive to increase flexigas and decrease imported fuel oil with benefit from the relevant price spreads up to the limit of flexigas circuit hydraulics and the coke gasifier air blower operation.

Recently implemented energy conservation projects across the Elefsina Refinery resulted in significant reduction in fired duty requirements increasing the incentive to substitute refinery fuel gas usage with flexigas on other units not previously considered for flexigas operation.

Elefsina Refinery Fuel System - Optimization Initiatives

Integrating a unit containing FLEXICOKING $^{\text{TM}}$ technology into the refinery allowed the optimization of fuel systems and disposition of fuel streams, as illustrated in the following three optimization initiatives by Elefsina Refinery:

Initiative #1 - In the initial configuration, hydrocracker sponge absorber gas, which is very rich in hydrogen (~70 wt percent H2) was burned in the hydrocracker unit fired heater. This valuable gas is ideal for recycling as steam reformer plant feed. The new configuration provides hydrogen recycling with net cash benefit from hydrogen plant feed reduction and provides room in the fuel gas pool for increased utilization of flexigas. The net benefit of this change is approximately five to seven million USD/yr.

Initiative #2 - The steam reformer plant furnace already uses pressure swing absorber (PSA) offgas as fuel. Flexigas heating value is similar to PSA offgas and, as part of this project, flexigas will replace refinery fuel gas in these applications. This project is currently under implementation.

Initiative #3 – Imported fuel oil is currently used as a backup fuel in the refinery. The intent of this third project is to replace fuel oil with natural gas as backup for boilers. Use of fuel oil as backup fuel requires a continuous minimum firing duty limiting potential for flexigas firing. Natural gas allows quicker and more reliable firing control eliminating the need for continuous low sulfur fuel oil firing. Most of the baseline fuel oil firing demand is then converted to flexigas. This project is currently under implementation.

CONCLUSION

FLEXICOKING technology is a commercially proven continuous fluidized bed process with integrated gasification that thermally converts heavy feeds to lighter liquid products, conventional fuel gas and a clean burning flexigas.

FLEXICOKING technology service include:

- Initial non-confidential consultations
- Development of licensing proposal
- Basic engineering package, including basic design specification and operating guide
- Engineering support during FEED and EPC stages
- Technology transfer, training and start-up support

Flexigas is a low cost fuel that is burned in commercially available burners in a wide range of fired heater and boiler applications and produces substantially lower sulfur and nitrogen oxides.

This paper illustrates how the incorporation of flexigas into a refinery fuel system can result in significant improvements to its economic and environmental performance as demonstrated in the Hellenic Petroleum Elefsina Refinery Upgrade Project.

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