TECHNOLOGIES FOR ENHANCING REFINERY GAS VALUE
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Abstract

The trend of processing more heavy and sour crudes, the shift in demand away from gasoline towards more distillate, and more stringent fuel qualities change the fuel and hydrogen balances in most refineries. Finding the right solution to managing fuel gas and hydrogen requirements has become essential for refineries to remain profitable. The refinery gas value is higher for hydrogen generation than for generating power and slightly lower than the value for using it as chemical feedstock. A combination of proven and new technologies is required to address refinery "fuel long" situations. Select refinery gas streams can be processed to recover hydrogen or as feed to SMRs. Cryogenic processing of refinery fuel gas to recover valuable products (hydrogen, olefins and LPG) is a viable option, and can be integrated with hydrogen post-purification technologies (e.g. PSA). Praxair has also developed a new patented refinery gas processor based on a short contact time catalyst that can reliably process refinery streams with high olefin and hydrocarbon with more than two carbon atoms concentration and convert them into SMR suitable feed. Different technologies that are suited to different refinery gas streams and how to optimize hydrogen recovery given differing energy and capital cost constraints is presented below.
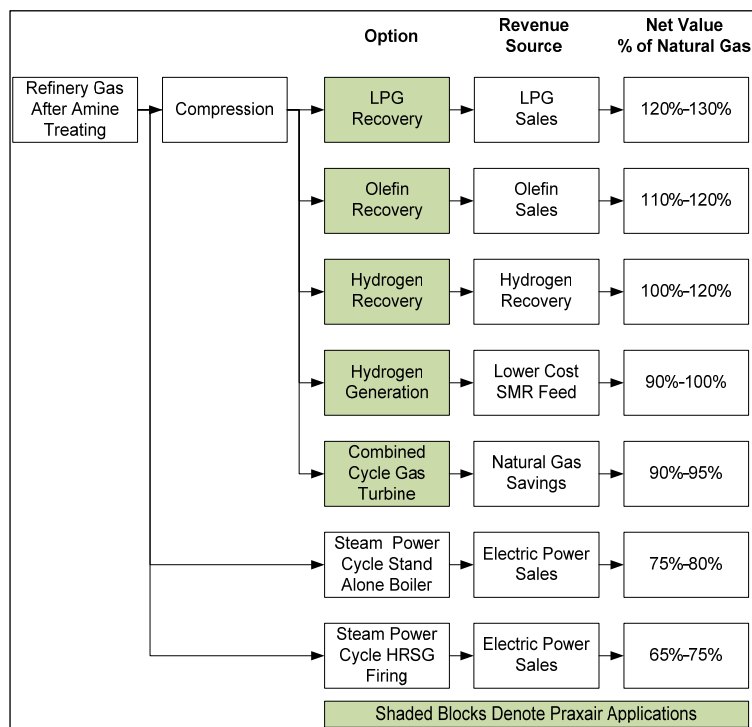
1   Introduction

Refinery fuel gas management has been recognized as a key element for optimum refinery operation. Refineries face pressure to increase their processing intensity in order to remain profitable and are seeking to increase their ability to process heavy and sour crude in order to achieve needed operational flexibility. These two main trends cause the demand for hydrogen to rise due to the increasing severity of hydroprocessing operations required to process the heavy and sour crude and yet meet the stringent product quality requirements. The increased processing severity has caused increased refinery gas (i.e. H_2, C_1-C_5) production, which exceeds in many cases the capability of the refinery to use it as fuel, forcing the refiner to change refinery operations to meet fuel gas constraints, produce and vent unneeded steam, flare fuel gas, or sell fuel at a discount. Furthermore, there is a shift in demand away from gasoline and towards more distillate. Some refiners are choosing to curtail their naphtha reforming capacity to address this market need. As a result, a significant source of hydrogen in a refinery is lost, thus widening the gap between hydrogen supply and demand. Refiners are likely to find themselves in a position with more fuel gas and less hydrogen, which has generated an increased interest in fuel gas management projects.

Managing the fuel gas system provides multiple benefits such as Increased operational flexibility and profitability, optimized hydrogen sourcing, reduced fuel demand, improved fuel gas quality, burner control and emissions and decreased CO_2 emissions. These are obvious direct benefits to upgrading the refinery fuel gas and implementing hydrogen

recovery systems, but there is also an indirect benefit to raising the overall hydrogen system purity. Rather than routing low-to-mid purity hydrogen to hydrotreaters, greater value from these process streams can be obtained by upgrading the hydrogen quality. Higher hydrogen purity will increase the purity of the recycle stream and reduce fuel gas production in the hydrotreating units. This can lead to both improved yields and performance or longer catalyst run lengths in hydrotreating units.

Another indirect benefit of better fuel gas management is that it is an enabler for other energy reduction projects. These projects generally lower the demand for fuel gas in various refinery operations, but the lack of an outlet for the "saved" fuel gas may become an impediment in the implementation of the energy conservation projects. Conversely, such projects achieve higher benefits if the "saved" fuel gas is utilized in a productive manner.

Refineries that are "fuel long" generally seek to export energy in the form of refinery fuel gas or look for other ways to extract value from the fuel gas system. Pressure Swing Adsorption (PSA) and cryogenic based separation methods are commonly used to recover hydrogen and hydrocarbons respectively from the fuel gas. Another approach is to use the gas as fuel for electric power generation, but this is usually the lowest value alternative. Fuel gas can also be used as feed to hydrogen plants (Steam Methane Reformers-SMRs). Generally such approaches are applicable to selected high-hydrogen, low-olefin streams (PSA systems or SMRs), or require chemical facilities nearby to use the recovered products (olefin recovery with cryogenic systems). Praxair economic analysis indic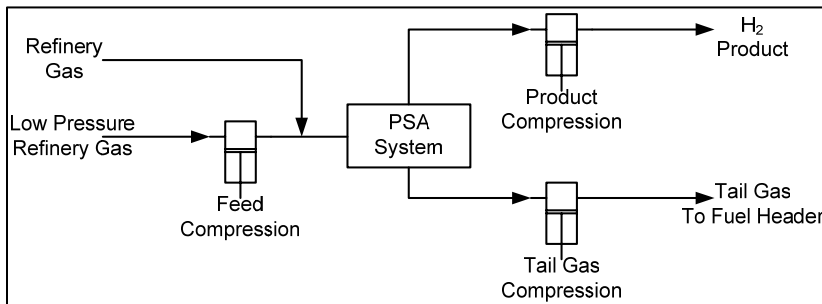ates that the value created by using refinery gas for hydrogen generation is higher than the value for generating power and slightly lower than the value for using it as chemical feedstock (Figure 1). Power generation from steam at refinery conditions is disadvantaged compared to power from other sources which tend to use higher efficiency combined-cycles. Refinery fuel gas is unsuitable as a feed to gas turbines with Dry Low NO_x (DLN) combustors. The typical DLN burner fuel specifications for hydrogen and C_2+ are 10% and 15% maximum, respectively. Refinery fuel gas likely has hydrogen and C_2+ content that exceeds these limits. Furthermore, olefins contained in the fuel gas tend to form soot and a minimal compositional variation is required to maintain NO_x performance of the DLN combustors. A common approach to get around these limitations is to use fuel gas as a supplemental fuel to the heat recovery steam generators (HRSG) in gas turbine cogeneration plant or as a fuel to the SMR furnace. However, this approach limits the amount of fuel gas that can be used and/or the value obtained from use of the fuel gas.

		Option	Revenue Source	Net Value % of Natural Gas
Refinery Gas After Amine Treating	Compression	LPG Recovery	LPG Sales	120%–130%
		Olefin Recovery	Olefin Sales	110%–120%
		Hydrogen Recovery	Hydrogen Recovery	100%–120%
		Hydrogen Generation	Lower Cost SMR Feed	90%–100%
		Combined Cycle Gas Turbine	Natural Gas Savings	90%–95%
		Steam Power Cycle Stand Alone Boiler	Electric Power Sales	75%–80%
		Steam Power Cycle HRSG Firing	Electric Power Sales	65%–75%
Shaded Blocks Denote Praxair Applications				

Figure 1: Refinery Gas Value for Different Applications Expressed as a % of the Value of Natural Gas

In addition to economic analysis technical analysis of refinery gas utilization opportunities is required to develop an appropriate solution. In the next paragraphs we discuss technical solutions utilizing existing technology as well as new technologies developed to address refinery gas with high olefin content.

2 Solutions for Fuel Gas Management

2.1 Integration with Hydrogen Production

There are different degrees of integration between hydrogen production and fuel gas management. Praxair has three distinct designs linking fuel gas management and hydrogen production that have been put into practice. The first design is a simple recovery of hydrogen. Figure shows a block diagram of a PSA based hydrogen recovery system. The refinery gas is compressed and then fed to a PSA. The tail gas is compressed and returned to the refinery fuel system, and the product hydrogen is compressed and delivered to a high pressure hydrogen consumer in the refinery. All three compression services are designed on a common reciprocating compressor frame. Praxair installed three 50% compressors to ensure high reliability.

Figure 2: Refinery Gas PSA Configuration

Simple recovery reduces the amount of on-purpose hydrogen that may be required to satisfy incremental demand. Other designs can integrate refinery streams into on-purpose hydrogen production. Praxair has implemented a second design where refinery gas can be used as a feedstock to a SMR hydrogen plant, with supplemental feed in the form of natural gas. In this specific example, the refinery gas feed is a light hydrocarbon stream with approximately 25% hydrogen by volume and 4% olefins. The refinery gas makes up approximately 45% of the total SMR feed, with the balance natural gas and contributes 42% of the total feed plus fuel to the facility. This configuration is shown in Figure 3. In addition to reducing the energy content required for on-purpose hydrogen production, this design also allows the hydrogen in the refinery gases, which is too low in concentration for economic PSA recovery, to be recovered the steam methane reforming process.

In the event that hydrogen recovery makes economic sense, but does not provide the total amount of additional hydrogen required by a refiner, a third design of PSA recovery integrated with on-purpose hydrogen production can be an attractive solution. Praxair is currently installing a facility that recovers hydrogen from a collection of refinery gases, and then uses the PSA tail gas as a SMR feedstock supplemented with natural gas as shown in Figure 4. This system leads to a high recovery of the hydrogen contained in the refinery gases because the PSA tail gas containing unrecovered
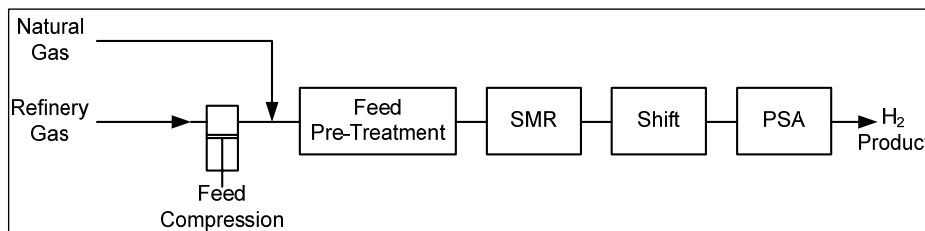
Figure 3: Refinery Gas as SMR Feed
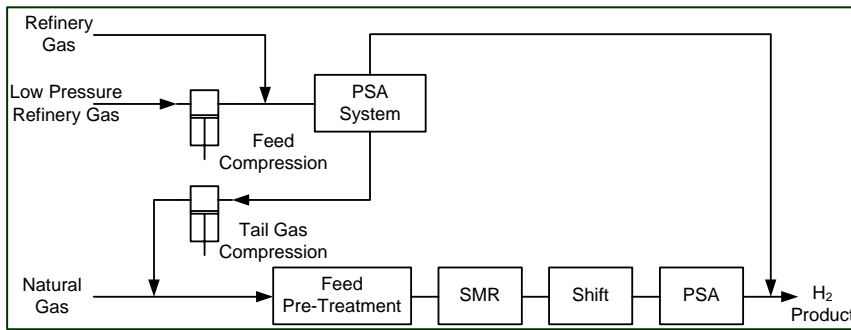
Figure 4: Integrated Hydrogen Recovery and Generation from Refinery Gas

hydrogen is further processed as SMR feed. In this case, the refinery gases again contribute 45% of the total SMR feed and 42% of the feed+fuel to the facility.

Recovering hydrogen from refinery streams decreases the need for on purpose hydrogen and can also reduce greenhouse gas emissions. Recovering 1 MMSCFD of hydrogen from the fuel header and displacing 1 MMSCFD of on purpose generation from a typical modern SMR will avoid the generation of approximately 22 Metric Tons of CO_2 (without fuel replacement of the recovered hydrogen). If the recovered hydrogen displaced on-purpose hydrogen from an older and less efficient SMR, the avoided CO_2 generation is even higher.

2.2 Hydrogen and Hydrocarbon Recovery with Cryogenic Systems

Recovering hydrogen and heavier hydrocarbons from refinery fuel gas can help refineries with both hydrogen and fuel costs. Cryogenic separation is typically viewed as being the most thermodynamically efficient separation technology. The higher capital cost associated with pre-purification and the low flexibility to impurity upsets has limited its use in hydrogen recovery.

However, it would be one of the first choices when higher value can be obtained from other products (olefins, LPG), especially when BTU removal from the fuel-gas system is of high priority.

Figure 5 presents the basic configuration of a two-stage partial condensation process for hydrogen recovery from refinery gases, with post purification via PSA and crude LPG recovery. The keys steps in this process involve first compressing and pre-treating the crude refinery gas (RG) stream before chilling (in BAHX1) to an intermediate temperature (-60 to -120 °F). This partially condensed stream is then
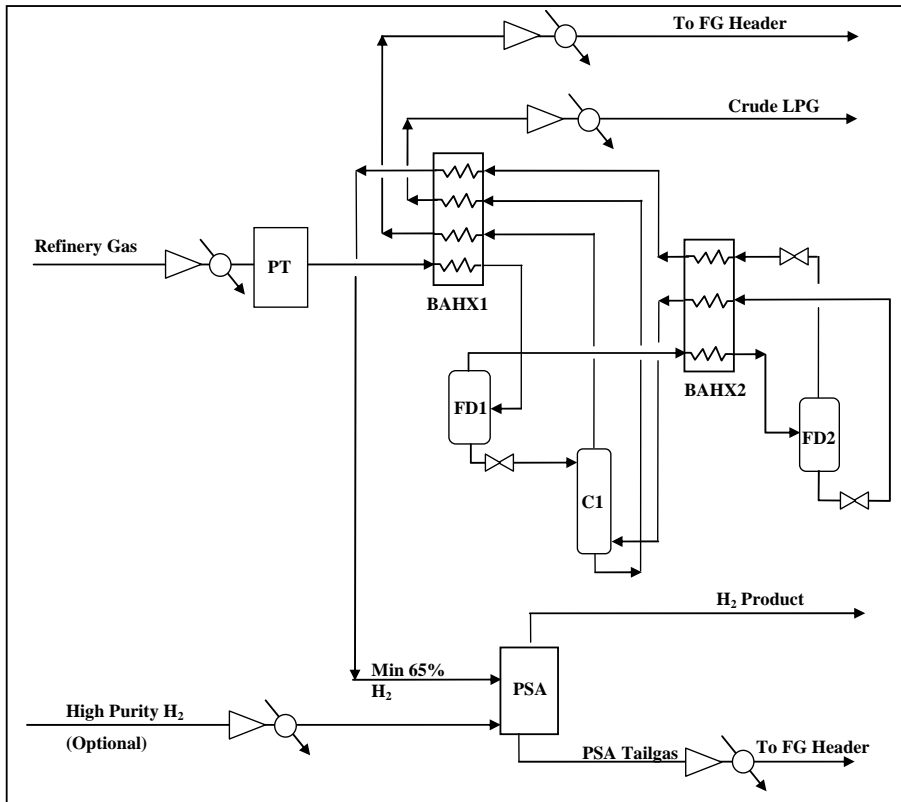
Figure 5: Integrated Cold Box and PSA Process for H_2 and Crude LPG Recovery

separated in a flash-drum (FD-1). The liquid stream from FD-1 is expanded through a Joule-Thompson (JT) valve to generate refrigeration and then is fed to the wash column C1. Optionally, column C1 can be replaced by a simple flash drum, with penalty on ethane/propane recovery. A crude LPG stream is collected at the bottom of the column, and a methane rich vapor is obtained at the top. The methane rich vapor is, after recovering refrigeration in BAHX1, sent to compression and then to fuel. The vapor from FD1 is further cooled in a second heat exchanger (BAHX2) before being fed to flash drum FD2, where it produces a hydrogen rich vapor and a methane rich liquid. The liquid is expanded in a JT valve to generate refrigeration, and then is sent back to BAHX2 to provide cooling. The resulting vapor is sent to column C1, and then processed as described above. The hydrogen rich gas is then sent to a PSA for further purification. The PSA tail gas is compressed and returned to fuel together with the methane rich gas from BAHX1. This cryogenic process/PSA integration can provide high purity hydrogen and LPG recovery from refinery gas.

2.3   Refinery Gas Processing for SMRs

Existing SMR integration technologies typically require refinery streams with high hydrogen and low olefin content [1] but the majority of refinery gas available does not meet these criteria. Refinery gas composition is typically highly variable with high olefin, C_2+ and sulfur content which makes it difficult to process in SMRs. Refinery gas composition is very different than natural gas, as shown in Table 1. Praxair has developed a new technology to address the limitations of typical refinery gas streams for hydrogen production and to permit their use in SMRs and Gas.

2.3.1   RFG constraints as SMR feed

Existing technology for treating refinery gas is based [1] on natural gas pretreatment and is not capable of reliably treating high olefin streams at a reasonable cost. Refinery gas used as feed to SMRs is preferably high in hydrogen, which can be routed to the PSA or low in olefins to facilitate treatment with conventional natural gas pretreatment technologies using a CoMo or NiMo catalyst. Much more readily available is refinery gas from a common refinery fuel header which is the outlet for by product streams from various refinery operations. As such it typically has high olefin content, high content of C_{2+} hydrocarbons and high compositional variability. High olefins present significant problems for a conventional hydrotreater, which operates within a narrow temperature window from about 550 to 750 °F. Olefin hydrogenation reactions are exothermic and each percent of olefins in the feed results in about 40-50 °F temperature rise in the hydrotreater. A refinery stream must contain less than 5% olefins to be fed to a conventional hydrotreater. Higher olefin concentrations can lead to temperatures that can cause catalyst deactivation and compromise the reliability of the SMR. In order to control the exotherm and avoid catalyst deactivation the refinery stream must be diluted either by the addition of natural gas or some of the treated gas from the hydrotreater must be cooled and recycled to the feed. The former reduces the amount of refinery gas that can be fed to the SMR and the latter necessitates the use of a high

Table 1: Typical Natural Gas and Refinery Gas Compositions		
Name	Refinery Gas	Natural Gas
	Mol %	Mol %
Hydrogen	28.00	-
Methane	28.00	95.00
C2+ parafins	24.00	3.50
Olefins	10.00	0.00
Nitrogen	3.50	1.00
Carbon Dioxide	3.00	0.50
Carbon Monoxide	3.50	0.00
Total	100.00	100.00
Sulfur ppm	25-250	5

temperature blower or booster compressor. Recycle compressors have been used but they introduce reliability concerns and increase capital and maintenance costs. Since compositional variations are very common with refinery gas streams, it is difficult to design and operate a hydrotreater with recycle to account for all possible variations. If off-spec refinery gas stream is detected the hydrogen plant must discontinue the use of the refinery gas to protect the SMR.
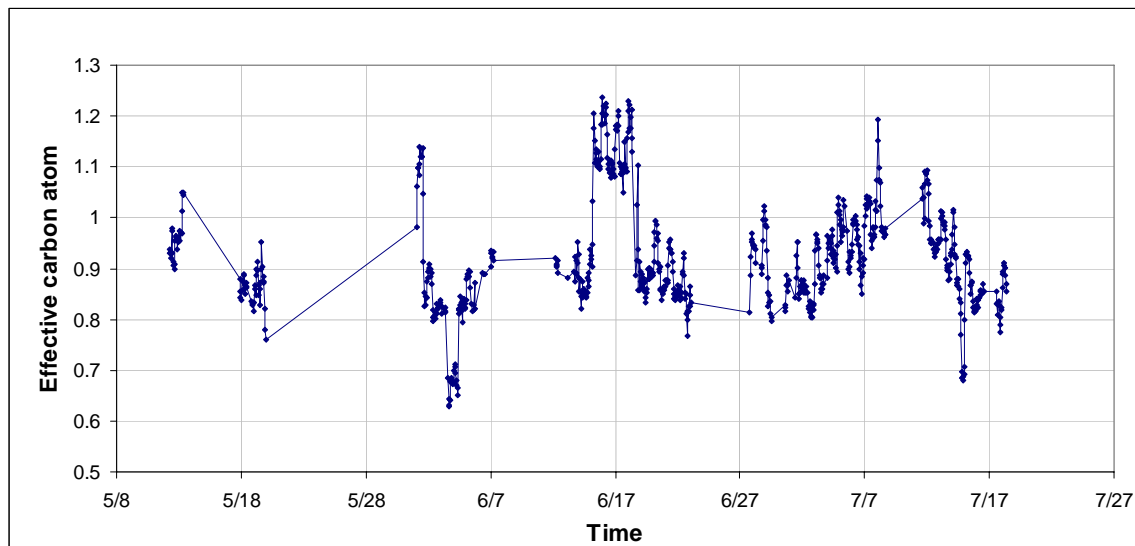
Figure 6: Refinery gas effective carbon atom variability

Refinery gas may also contain C_2+ hydrocarbons (e.g. ethane, propane) in amounts that far exceed what is contained in natural gas. If the hydrocarbons in refinery gas are represented by the formula C_xH_y then x is an effective carbon atom number that can provide information about the content of C_2+ hydrocarbons. For methane x=1 so the higher x is for a given refinery gas composition the higher the amount of C_2+ is in the refinery gas. The effective carbon atom number can be calculated by the refinery gas composition. Figure 6 depicts the effective carbon atom variation of refinery gas at a U.S. refinery over a period of about two months. A significant variation can be observed in both short term and longer term composition which necessitates careful design of the SMR control system. To accept these streams in a SMR a prereformer or an alkalized reforming catalyst can be used which may not be an option for existing SMRs. Alternatively the steam to carbon ratio may have to be increased to a higher value which depends on the C_2+ hydrocarbon content; however, this will reduce the thermal efficiency of the plant. Refinery gas composition variability must be taken into account in the plant design to prevent situations that compromise the reliability of the SMR, such as operating with steam to carbon ratios that are either too low (catalyst coking) or too high (energy loss). Variable composition can lead to swings in SMR's operating performance. A highly responsive analysis technique such as a mass spectrometer or calorimeter would be required for predictive control. Although with advances in controls and analytical techniques these issues can be addressed with proper design it is still desirable to have a technology that can eliminate or reduce the severity of these problems.

2.3.2 Refinery Gas Processing (RGP) Technology

Praxair's refinery gas processor is based on a novel short contact time catalyst capable of operating at a space velocity of at least 50,000 hr^{-1}. This catalyst has an extended

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temperature window of operation (300-1600 °F) which permits operation with levels of olefins previously unachievable without feed dilution. The catalyst is in monolith form and can be on a metallic or ceramic support. A precious metal like rhodium or platinum is deposited on the monolithic support. The catalyst is derived from catalytic partial oxidation type catalysts pioneered by Schmidt et al [2] at the University of Minnesota. These catalysts have been used in partial oxidation of methane to produce synthesis gas [3] and for oxidative dehydrogenation of paraffins to olefins (e.g. ethane to ethylene). It has been discovered [4, 5] that the same catalyst is very effective in the hydrogenation of olefins.

Based on this discovery a process that can operate under hydrogenation or oxidation conditions with the same catalyst was developed. Firstly in hydrogenation mode (no oxygen) the reactor converts olefins to paraffins with the contained or supplemental hydrogen but with a much wider operating temperature window compared with conventional technology. The RGP permits utilization of refinery gas streams with high olefin content and high olefin variability. Secondly with the addition of small amounts of oxygen (up to 10% of RGP feed) and steam (up to 1:1 steam to carbon ratio) the reactor can operate in a prereforming mode that reduces the amount of hydrocarbons with two or more carbon atoms in addition to reducing olefin levels. By tuning the oxygen consumption, the refinery gas composition variations can be reduced thus improving the operation of the SMR. The same reactor can be used in both operational modes and no shut-down is required to transition between modes. The dual operation can expand the type of refinery gas composition that can be routed to the SMR and can replace two unit operations, a hydrotreater and a prereformer. In addition, RGP offers higher reliability due to the elimination of the recycle gas compressor and the ability to regulate refinery gas variability. The simple and flexible flowsheet makes it easier to retrofit existing SMRs to operate with refinery gas as a feed.
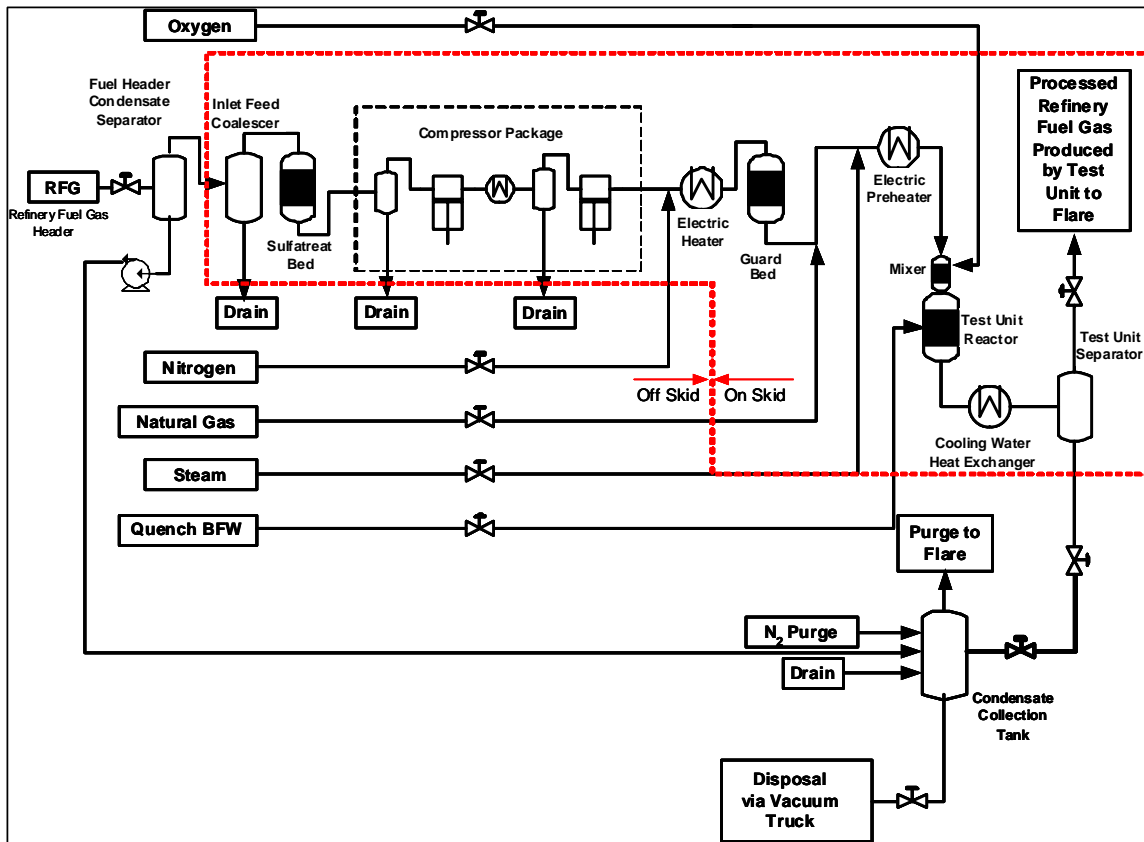
2.3.3 RGP Performance Results

Extensive laboratory testing was undertaken at Praxair's Technology Center (2005-2007) with simulated refinery gas to perform parametric analysis, develop efficient operating conditions, select appropriate catalyst and test the ability to operate in hydrogenation mode or prereforming mode. Since it is not possible to simulate all of refinery gas characteristics in the laboratory a pilot test unit was designed and built at a refinery location. The design and construction was done by Praxair's

Figure 7: RGP Pilot Unit at a US Refinery

engineering. The pilot unit picture is shown in Figure 7.

A process flow diagram of the pilot unit is depicted in Figure 8. The refinery gas was received from the refinery gas fuel header and passed through a condensate separator to remove any free liquids. Then the fuel gas was passed to a coalescing filter before a bulk sulfur removal bed. The reduced sulfur feed was then compressed with a two stage reciprocating compressor to about 220 psig. The compressed gas was heated and then

Figure 8: RGP pilot unit process flow diagram

passed to a finer sulfur removal bed. The gas was then preheated to the desirable temperature (up to 700 F) before send to the reactor. The reactor product was cooled with boiler feed water injection and after liquid separation it was send to the flare. Optional oxygen, steam and natural gas could be added to reactor feed for specific tests. Samples from various parts of the process were send to the analytical system that comprised a calorimeter, a gas chromatograph, a sulfur analyzer and oxygen analyzers which were housed in a separate enclosure.

The pilot unit was designed to treat 5000 scfh of refinery gas from the refinery fuel header. The pilot unit operated from 2007-2009 for more than 6000 hours and was able to demonstrate that the technology is uniquely capable of treating refinery gas. The unit operated with up to 17% olefins in the feed and up to 450 ppm organic sulfur. The unit was able to respond to feed variability, demonstrated acceptable catalyst life, switched between oxidation and hydrogenation mode seamlessly, demonstrated safe operation and increased hydrogen production in prereforming mode.

Figure 9 presents the feed and product olefin composition for a period of two months with significant olefin variations in the feed (4-17%) but with product composition that remained below 1% for the majority of time. Only when the unit was operated with very high propylene in the feed did the exit olefin composition approach 2% at the high reactor exit temperature (1100 °F), where propylene conversion was limited by thermodynamic equilibrium. The level of olefins achieved at the exit of the RGP can be easily handled by the SMR hydrotreater, and allows for reliable plant operation with refinery gas feed. Praxair is finalizing the parameters that allow the RGP to be used to increase hydrogen production and displace a pre-reformer.

Testing has demonstrated pre-reforming activity in oxidation mode and economic analysis indicates that an RGP system could have a substantial capital advantage when compared to a
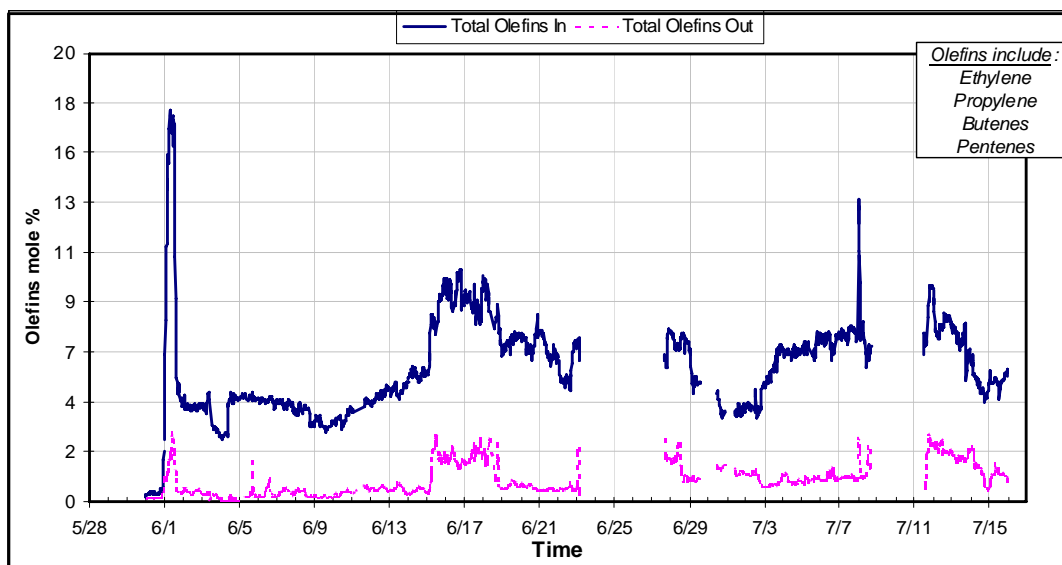

Figure 9. RGP Feed and Product Olefin Composition from Pilot Plant Experiments

pre-reformer in a debottleneck scenario.

2.3.4 Kinetic Model

Analysis of the RGP alpha plant data showed that several parameters affected the reactor performance when operating in hydrogenation mode. The ROG feed gas temperature and concentration of olefins, type of olefin, hydrogen partial pressure, and total sulfur had the greatest effect on the olefin conversion. Space velocity and reactor pressure also impacted the product distribution. An empirically derived global kinetic reaction model was constructed that incorporated all of these variables. As shown in Figure 10 there is a good match between the experimental data and the model predictions.
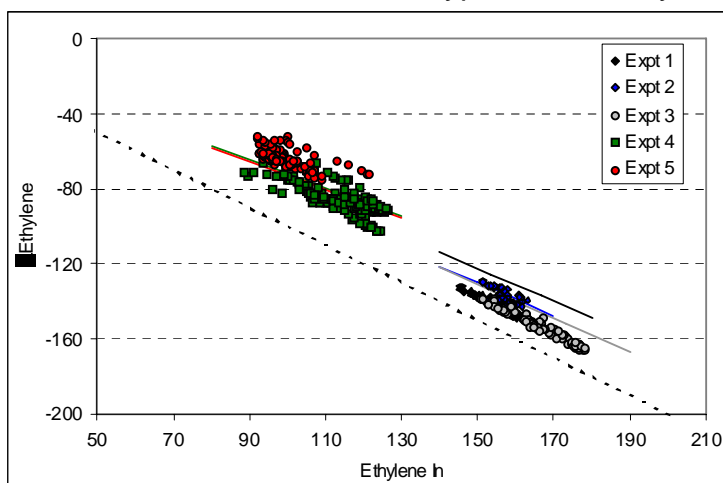
Figure 10. Plot of change in ethylene scfh as a function of the inlet ethylene comparing experimental results (points) against model predictions (lines) for five different experimental conditions.

2.3.5 Other RGP Applications

The RGP can be used in oxidation mode not only to eliminate olefins but to increase the hydrogen content of the refinery gas and reduce the amount of C_2+ hydrocarbons. This can be exploited advantageously by either reducing the heat load of the SMR to produce the same amount of hydrogen or by maintaining the same heat load and increasing the amount of hydrogen that can be produced. Since the system can operate in either hydrogenation or oxidation mode with the same reactor, the oxidation mode with increased hydrogen production could be used at times of high hydrogen

demand, and hydrogenation mode operation with normal hydrogen production the rest of the time. Praxair estimates that 10-20% production increase can be achieved in oxidation mode in an existing plant depending on refinery gas composition and other hydrogen plant bottlenecks.

In addition to using RGP for SMR feed treatment, the technology could also be used to treat refinery gas so it can be used in gas turbines as substitute natural gas. Gas turbines with DLN combustors can be designed to operate on refinery gas provided the amount of heavier hydrocarbon and hydrogen are controlled. High levels of higher molecular weight hydrocarbons, especially olefins, can form carbon within gas turbine combustors and result in erosion and fouling of gas turbine components and the emission of "smoke" in the gas turbine exhaust. Hydrogen and olefins can also ignite prematurely and compromise the gas turbine DLN combustor. The RGP operating in hydrogenation or oxidation mode can control the level of olefins, C_2+ hydrocarbons and hydrogen within acceptable levels.

3   Conclusions

The following staged approach is used by Praxair to assist refineries in their efforts to obtain cost reduction, profit improvement and regulatory compliance by better fuel gas and hydrogen management:

- Perform an evaluation of the overall hydrogen and fuel/energy systems which will assist in identifying potential value-added opportunities;

- Work closely with the refinery to fine-tune and validate the opportunities identified;

- Develop the solution, based on refinery's feedback and final optimization

A combination of proven and new technologies is available to provide solutions to refinery "fuel long" situations. If refinery gas with high hydrogen and low olefins is available then a PSA or a conventional SMR can be used as outlets. If high olefins, variability and high hydrocarbons are concerns then RGP technology is available to address these issues. If hydrocarbon recovery is desired a cryogenic system can be designed to simultaneously produce LPG or chemical feedstock and high purity hydrogen.

A new technology has been developed to allow use of refinery gas streams with high olefin concentration in SMRs and gas turbines. Using a short contact time monolith reactor olefins can be reduced to levels that are manageable by the SMR HT. This new technology can also be used to control feed composition variations and to optimize hydrogen production.

4   References

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