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## Scientific & Technical Report

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### **Removal of Black Powder and Other Contaminants in LPG/LNG Furnace Feeds**

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## Abstract

Hydrocarbon feedstock (gas, supercritical fluid, or liquid) to ethylene crackers may contain significant levels of corrosion products, or water and salts. Iron oxides/sulfides and sodium are well known coke promoters. They reduce the run length of the furnaces, which results in loss of ethylene production, shortened furnace tube life, higher maintenance costs, and undesirable side products such as CO in cracked gas. The term “black powder” is applied to corrosion products widely prevalent in pipelines that transport natural gas and hydrocarbon feedstocks. If there is black powder in a pipeline, then pigging operations will aggravate the problem.

Many separation technologies have been employed to remove solids from the pipelines but they suffer from poor performance in this demanding application. This paper discusses the use of highly efficient, longer lasting filters that have been extensively used in the Middle East in recent years to mitigate black powder issues. The paper also discusses a recent commercial filter design that incorporates a two-stage separation with a high performance cyclone and particulate filters in certain cases. The presence of liquid water/hydrocarbons in the pipelines carrying gas is also detrimental to the process. Liquid/gas coalescers containing proprietary surface treated materials have been employed to remove this contaminant.

Besides furnace feed gas, fuel gas to the furnace can also contain contaminants. Fuel gas used as the regeneration gas for the molecular sieve driers may contain significant amounts of oil. This contaminated fuel gas causes fouling of the furnaces’ burner nozzles. This results in frequent and expensive burner tip cleaning and loss of furnace efficiency, especially critical for low NO<sub>x</sub> burners. The use of liquid/gas coalescers to remove these hydrocarbon contaminants will also be discussed.

## Introduction

Black Powder is a common corrosion related contamination found in pipelines transporting LPG, LNG and hydrocarbon condensates. Studies<sup>1</sup> of particle size distribution have shown that a majority of the contaminant is very fine and sub-micron in size. Previous studies<sup>2</sup> have shown that they consist primarily of iron oxides. The presence of sour gas accelerates the formation of mixtures of iron sulfide and iron oxides. Black Powder is a global phenomenon and occurs in pipelines. Elevated temperatures appear to increase the formation of these solids. Additional non-corrosion related solids such as sand or silt may also be present in the gas stream. Characteristics of black powder solids are:

- Very fine contaminants, forming agglomerates in micron size range – typically **1-10** micron
- Easy to transport, difficult to capture
- May be pyrophoric
- Need for appropriate handling and disposal procedures

“Pipeline rouge” is another term commonly used to describe corrosion products retrieved from pipelines, but the composition is similar to black powder, only the color is red instead of black. The predominant compound in pipeline samples is typically magnetite, which is black in color. Minor components such as greigite ( $\text{Fe}_3\text{S}_4$ ), siderite ( $\text{FeCO}_3$ ), or hematite ( $\text{Fe}_2\text{O}_3$ ) probably give pipeline rouge its color.

In addition to these solids, the gases may pick up hydrocarbon and aqueous contamination from storage in the pipelines. They are present as fine droplets or aerosols in the gas phase. The presence of water in liquid phase promotes corrosion reactions. The presence of oxygen, hydrogen sulfide and carbon dioxide accelerate the corrosion reactions in the steel pipelines. Pigging operations have resulted in enormous amounts of black powder (500-5000 kg) being removed from scraped pipelines.<sup>2</sup>

## Impact of Black Powder

The presence of black powder and aerosols in the incoming LNG/LPG to ethylene furnaces can have a detrimental effect on the performance of the furnaces. Many problems have been documented, leading to shortened furnace run lengths and expensive maintenance issues. These include:

- Accelerated coking reactions in the tubes and fouling in the convection section
- Formation of CO in cracked gas
- Loss of furnace capacity during pigging operations of the pipelines
- Severe corrosion resulting in frequent replacement of damaged furnace tubes

In natural gas pipelines, the problems caused by black powder and water/hydrocarbon have been recently documented.<sup>3</sup> Some of them include:

- Process upsets such as off-spec product with high water in condensate/crude
- Foaming in amine sweetening units and glycol dehydration units
- Equipment failures leading to fouling and plugging of reboilers in the fractionation plants
- Poor accuracy of meters/valves
- Failure of critical instrumentation
- Safety and environmental issues such as gas releases

## Measurements of Black Powder

Isokinetic sampling<sup>1</sup> offers the best practice to remove representative particles as they are in the gas stream under operating conditions. An in-line isokinetic probe combined with a disc membrane is used for gas sampling from the pipelines and the collected gas is analyzed for Particle Size Distribution. The equipment contains a probe that is inserted into the process pipeline at the appropriate location and has a flow meter and control valve to adjust the flow rate to maintain the same flow rate of the gas in the sampling apparatus as the main pipeline. The probe can be inserted at different lengths to sample the gas at different locations within the diameter of the pipe (near the walls or in the center).

### Particle Size Distribution (PSD)

Process gas or liquid is passed through a test membrane rated at 0.1 micron in gas service to collect solids. The membrane can be evaluated manually using an optical light microscope for particle size analysis. It can also be automatically evaluated using an Energy Dispersive X-ray probe of a Scanning Electron Microscope (EDX-SEM) to scan the membrane. The particle sizes are measured to 1 micron.

### Total Suspended Solids (TSS)

Pre-weighed 47 mm diameter test membranes rated at 0.1 micron in gas service are used to collect solids from the process pipeline. A sufficient amount of gas or liquid is passed through pre-weighed membranes to collect solids in the field and the membranes are then transported to the lab for final analysis. The TSS is reported in terms of ppmw or gram/MMSCF.

### Analysis of LPG Pipeline Deposits

Deposits retrieved from Dow LPG and propane pipelines contain predominantly reduced iron oxide (magnetite) with minor amounts of other iron compounds like iron carbonate (siderite,  $\text{FeCO}_3$ ), and iron sulfide (greigite,  $\text{Fe}_3\text{S}_4$ ). X-ray diffraction identified the major crystalline product as magnetite ( $\text{Fe}_3\text{O}_4$ ) in all of the samples. Other crystalline phases in minor amounts are iron carbonate, iron oxide (hematite,  $\text{Fe}_2\text{O}_3$ ) and magnetic iron sulfide or greigite ( $\text{Fe}_3\text{S}_4$ ). For LPG or propane stored in a brine well, it is also common to find salt (NaCl) at minor levels, indicating carryover of brine from the well.

## Filtration/Separation Techniques Used

Different solutions have been commercially devised in the natural gas industry and in the feeds to ethylene gas crackers to mitigate the impact of black powder and to remove the water/hydrocarbons from the gas. A brief description of these technologies is provided below. There are four (4) identified product platforms.

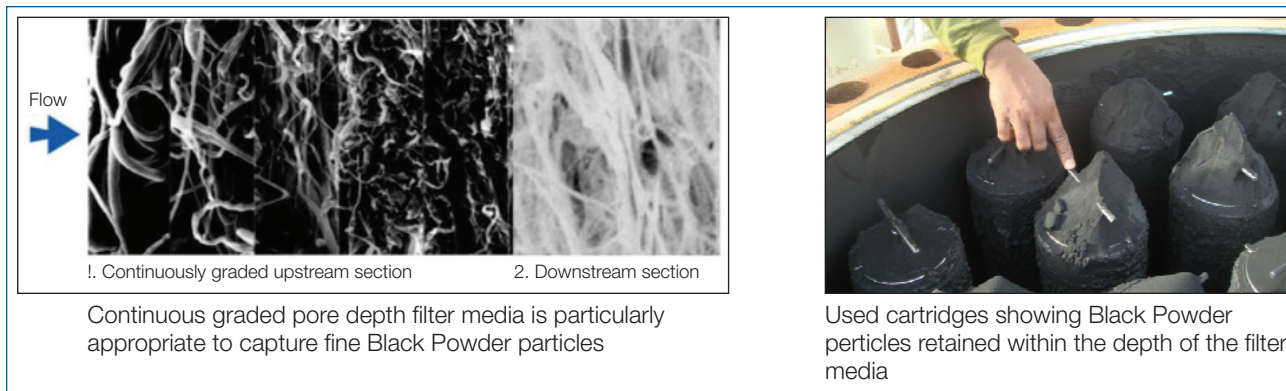
1. Depth and pleated cartridge filters to remove solid contaminants
2. Systems of cyclonic devices in combination with cartridge filters
3. Liquid/gas coalescers to remove contaminants such as water and hydrocarbons
4. Liquid/liquid coalescers to remove water/hydrocarbons assuming that the gas is in a supercritical state or liquefied single phase flow regime

### Depth and Pleated Cartridge Filters to Remove Solid Contaminants

A number of different filter materials are available. Cellulose, glass fiber and polypropylene are the most common types. It is important to capture black powder contaminants in finely rated “absolute” cartridge filters for maximum performance.

An important distinction exists between how filters are rated, and the terms “nominal” and “absolute” which can give very different performance for a filter labeled with the same micron rating. Nominal filters are unreliable and are not subject to the same quality control. The consequence is that particles larger than the claimed removal rating pass through the filter. In some cases, nominal filters can collect contaminants and then as the pressure drop increases, release the trapped materials back into the stream. Absolute filters are tested by using particle counters to measure efficiency based on a distinct particle size cut off and manufactured to more demanding specifications. They are designed to not release any trapped contaminants up until the design terminal pressure drop.

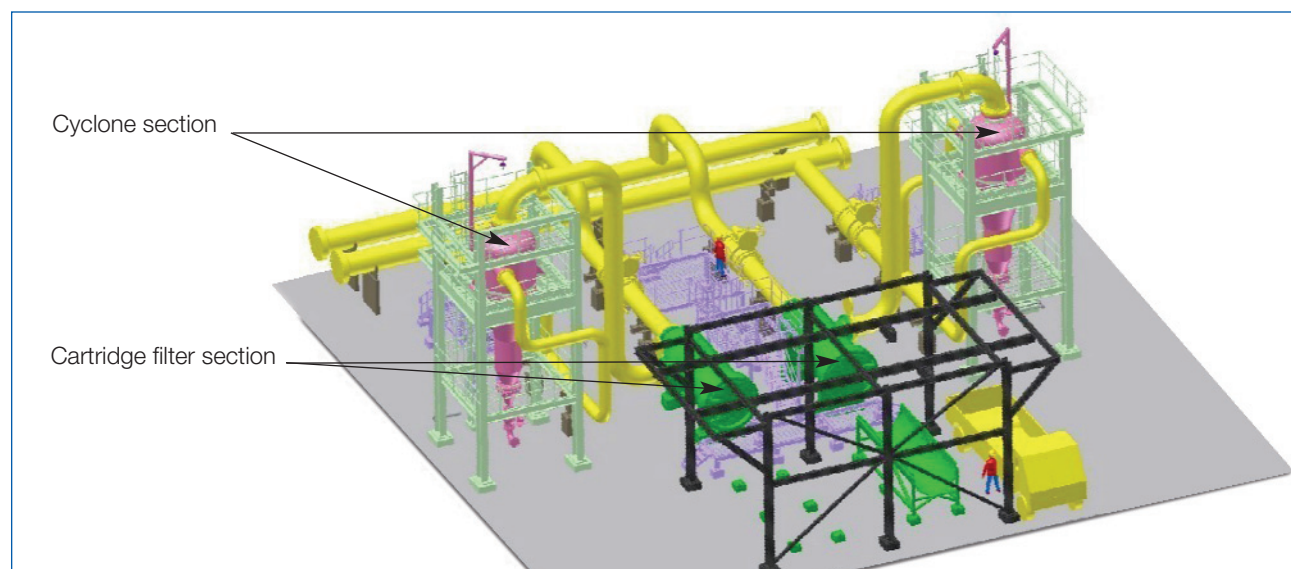
An example of the use of absolute depth filters that are coreless (low disposable cost) is shown in **Figure 1**. It is a high efficiency absolute filter with a rating of 1-10 microns.



**Figure 1:** How an Absolute-rated Filter Performs to Capture Black Powder

## Systems of Cyclonic Devices in Combination with Cartridge Filters

Combinations of cartridge filters and Cyclone Separators – Cyclo-Filter Systems<sup>3</sup> – have also been employed for natural gas pipelines experiencing significant amounts of suspended solids in the feed. This is common in the LNG pipelines in the Middle East but perhaps not required for ethylene plants which have lower solid levels in the feed. It consists of a two-stage separator system – a low velocity cyclonic system followed by an absolute-rated depth filter. The cyclone system removes particles >5-10 microns in size and the cartridges downstream of the cyclone product remove the particles to the required specification. The cyclone generates low pressure drop (a few psi) since it operates at lower velocity flow. This combination is capable of handling high solid loadings, including slugs. An example is shown in **Figure 2**.



**Figure 2:** A Cyclo-Filter System

## Liquid/Gas Coalescers to Remove Contaminants Such as Water and Hydrocarbons

Water/hydrocarbon removal in the incoming gas is best achieved via a high-efficiency liquid-gas coalescer if the contaminant is present as aerosol droplets. There are many existing mechanical separation technologies that are utilized, depending on the droplet size to be removed from the gas phase. These include knock-out drums, demister pads and vane packs as well as liquid/gas coalescers. **Table 1** shows that a conventional separation device may not be adequate in effecting a clean separation.

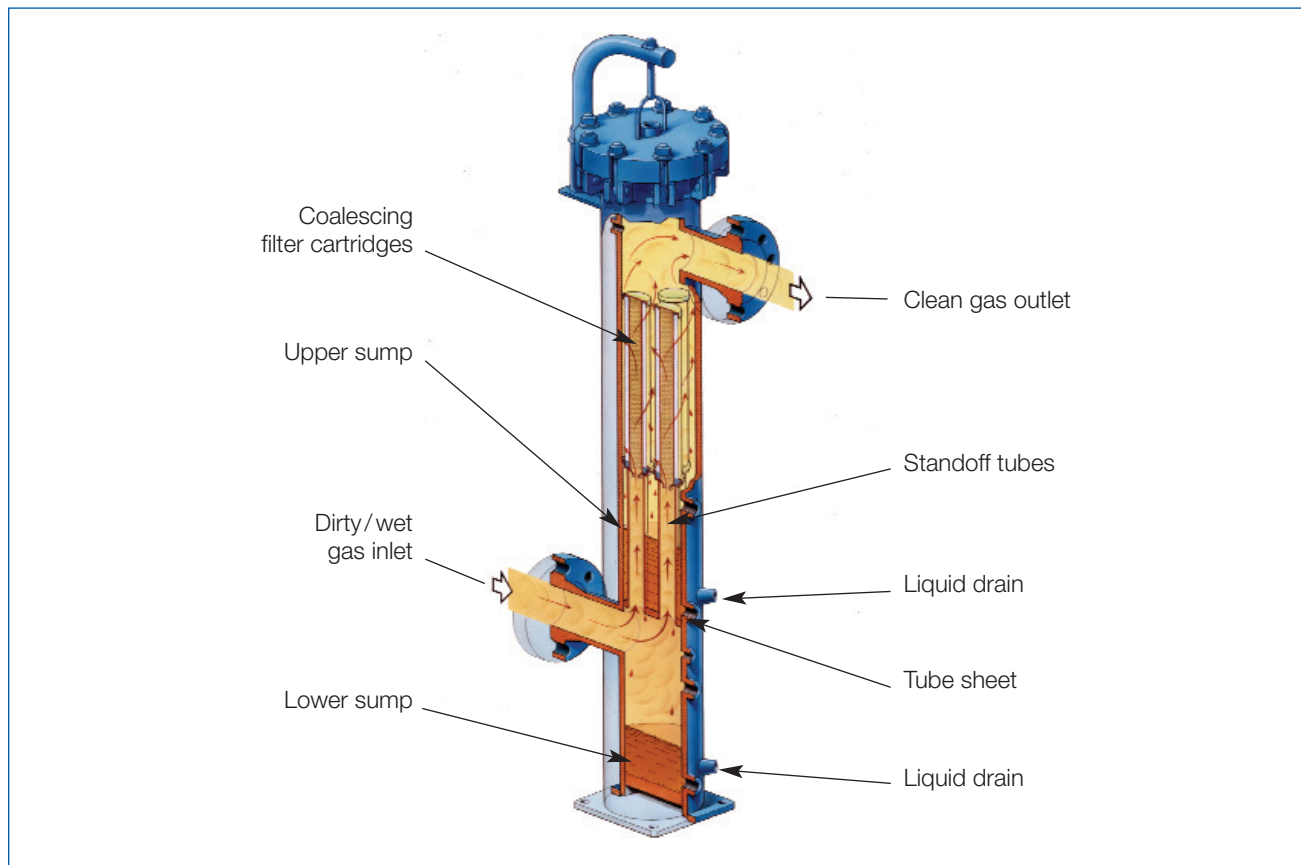
**Table 1:** Comparison of Separation Equipment

Separation Equipment	Drop Size Removal	Separation Mechanism	Sensitivity to Flow Rate Variations
Knock Out Drum	> 300 $\mu\text{m}$	Gravity	Medium
Cyclonic Separator	> 10 $\mu\text{m}$	Centrifugal	Medium
Vane Pack	> 10 $\mu\text{m}$	Inertial impaction	Sensitive
Demister Pad	> 5-10 $\mu\text{m}$	Inertial impaction	Sensitive
<b>Pall's High Efficiency Coalescer</b>	<b>&gt; 0.1 <math>\mu\text{m}</math></b>	<b>Diffusion and direct interception</b>	<b>Insensitive</b>

Liquid/gas coalescers operate on the principles of diffusive capture. Proprietary surface treatment enhances the clean separation between the droplets and the gas and promotes liquid drainage. This high-efficiency, vertically mounted separator can demonstrate a particle filtration rating >0.1 microns and the downstream aerosol content in the clean gas can be as low as 0.01 ppm. It is a versatile device and can handle liquid loadings of >100 ppm. If the liquid loadings are very high, it is possible to use a combination of conventional separation with coalescence.

Pilot units of liquid/gas coalescers are available for use for field tests with the gas streams. A slipstream of the gas in the pipeline at a constant flow rate is passed through the pilot unit and the condensed liquid accumulated in the bottom sump is measured and analyzed. The test is done over a few days to collect representative data.

A liquid gas coalescer is shown in **Figure 3**.

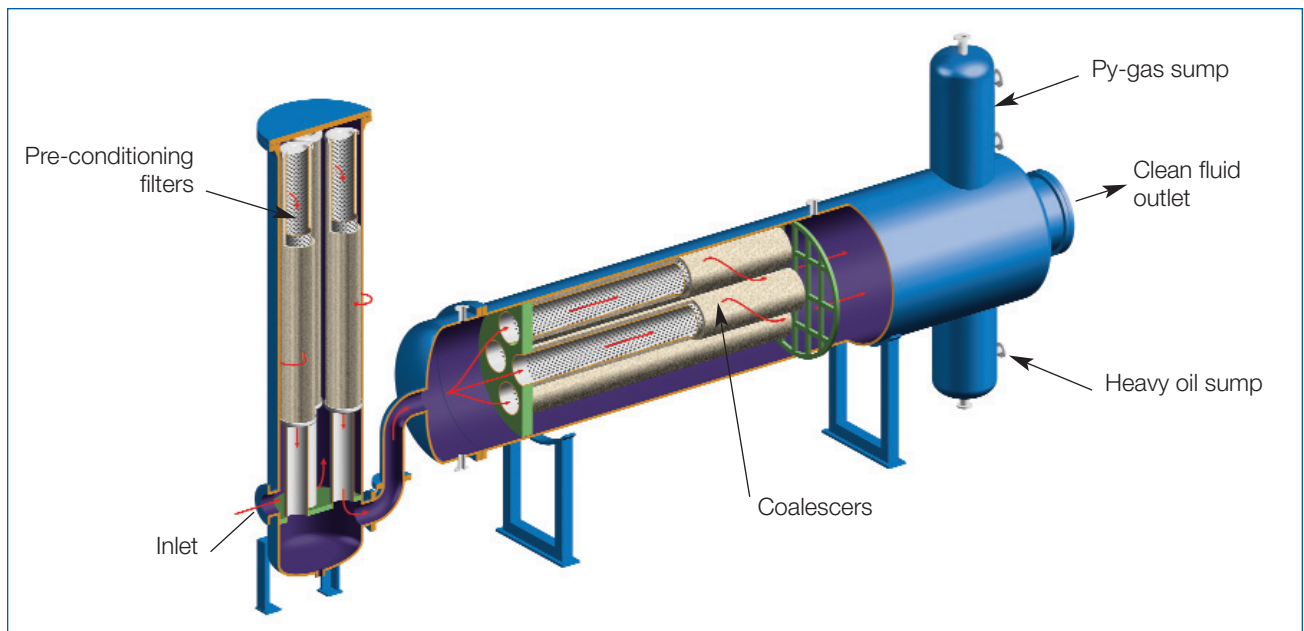


**Figure 3:** Liquid/Gas Coalescer

## Liquid/liquid Coalescers to Remove Water/Hydrocarbons

Liquid/liquid separators are also used in cases involving removal of a discontinuous liquid phase from another liquid. An example of this application would be to remove brine and/or hydrocarbons from liquefied natural gas feeds that are introduced into ethylene cracking furnaces. There is a prefilter prior to the liquid/liquid coalescer to remove black powder solid contamination to 10 microns or below. The prefilter will protect and prolong the life of the coalescer, which breaks the emulsion of the contaminants in the liquefied gas. Oil and grease numbers < 20 ppm in the coalescer outlet are achieved with a proprietary surface treated coalescer and this will enhance the run lengths of the furnace. An example of a horizontal liquid/liquid coalescer is shown in **Figure 4**.

Pilot units are also available and used for liquid/liquid coalescence. A slipstream of the two immiscible liquids (under high/supercritical pressure) containing solid contaminants is passed through the prefilter and then separated by the surface treated coalescer. The quality of the separation is measured with oil and grease measurements on the product liquid. The run length of the prefilter cartridge is a measure of its efficiency in removing suspended solids that would otherwise foul the coalescer element.



**Figure 4:** Liquid/Liquid Coalescer with Prefiltration

## Case Histories from Ethylene Feed Contaminant Removal

### Case Study 1

A gas cracker in Australia was only equipped with a knock out drum ahead of the furnaces. Flow rates of ethane gas in the feed was 10,900 m<sup>3</sup>/hr (9250 MMSCF/day) and the line pressure was 220 psig at a temperature of 68°F. Slugs of iron sulfides and oxides in the ethane feed (black powder) were causing two significant problems:

- CO levels in the cracked gas exceeded 7000 ppmw and resulted in off-spec ethylene
- Time between furnace decokings decreased by as much as 70% and it took several furnace decokings to recover normal operation

A high surface area pleated filter assembly containing seven cartridges was installed in the pipeline. The removable filter bundle was installed in the existing pig receiver vessel. Change out frequency was observed to be twice a week during pigging operations. The ethylene product was no longer off-specification and there was no furnace reduction in run times as well as no furnace fouling. The return on investment was as low as three months. The micron rating for removal from the gas phase was 99.9% @ 0.3 microns.

### Case Study 2

A world scale ethylene plant (gas cracker) was commissioned in the past five years in the Middle East and uses ethane as feedstock. The licensor/process engineering company designing the plant anticipated large quantities of black powder in the feed ethane gas since it was transported in hot pipelines that were subjected to pigging operations. Hydrocarbon liquids were not expected to be present in the gas. They decided to install disposable cartridge filters to protect the furnaces. The following parameters were given to design the filter treatment:

- Flow rate of feed gas: approximately 160,000 m<sup>3</sup>/hr or 135 MMSCFD/day
- Operating pressure: 20 bar/290 psig
- Maximum operating design temperature: 82°C/219°F
- Design pressure drop across filter: should not exceed 1 bar/14.7 psig

The solution was to use a vessel with 19 polypropylene depth filters (without a center core). The filter had an external diameter of 6 inches and a length of 40 inches. The maximum operating pressure drop did not exceed 15 psig at 82°C. This product captured the black powder throughout the depth of the filter and was easy to change out and discard, after the terminal pressure drop was reached. The performance was good and it lasted six months on average after the performance was stabilized. It efficiently captured solids – 99.9% @ 0.3 micron in size. The furnace run length was not impacted since the black powder was almost completely removed by these filters.

### Case Study 3

In another large Middle East ethylene plant (gas cracker), ethane was being supplied in a supercritical state under high pressure as feed to the furnaces. The pipeline was nearly 100 km long and suffered from high levels of black powder. Analysis showed the contaminants to be predominantly iron sulfide and oxide. The flow rate in the dense phase was 137 MMSCF/day.

A highly pleated filter assembly (42 elements/vessel) was installed with a surface area of 54 sq ft/cartridge. It provided 2 micron filtration of particles in liquid phase with a filtration efficiency of 0.3 micron at 99.9% efficiency in the gas phase. The filter medium was resin bonded glass fiber. However, it was undersized for the volume of full scale flow and the suspended solids level in the dense phase was high. Initially, the filter assembly was changed once a week. However, due to improvements upstream in the quality of the feedstock, the performance of these filters improved substantially. These changes involved passing the gas through Cyclo-Filter Systems, shown earlier in **Figure 2**. The change-out rates are currently in the range of 3-6 months. In the latest configuration, a vessel with 140 cartridges of the same filter will be installed soon to augment the removal of black powder. It must also be noted that the technical challenge was created by presence of solids alone and no liquid contamination (hydrocarbon or water) was observed in the feed.



## Case Study 4

A downstream petrochemical plant in the Middle East was using natural gas from the gas grid. The flow rate was 112,000 m<sup>3</sup>/hr or 95 MMSCF/day. A knock out drum and nominally rated 2 micron cartridge filters were originally installed to capture black powder in the pipeline and prevent it from clogging the downstream process units. However, it was found that the downstream compressor was damaged and there were unscheduled shutdowns of the process units. The nominally rated cartridges were being replaced every 1-2 weeks.

A root cause analysis was carried out at the plant level. One measure was the particle size distribution of particles in the gas stream before and after the existing filter. It was discovered that the efficiency of filtration was poor and many large particles were found downstream of the filter. The plant finally installed “absolute rated” coreless depth filters of polypropylene with tapered pore structure. Thirty (30) elements in the housing provided sufficient area for filtration of the contaminants.

After six months, performance tests on total suspended solids (TSS) were conducted on the gas upstream and downstream of the filter<sup>3</sup>. The TSS was reduced by 97%, from 0.61 ppmw to 0.01 ppmw. Excellent performance was achieved as the filters lasted 20 months before replacement and they provided the desired protection to downstream units. The total cost of filtration dropped to 10% of the previously incurred costs.

## Removal of Contaminants from Fuel Gas to Furnaces

Feeds to the ethylene furnaces include fuel gas for the furnace burners. While all burners are susceptible to fouling, a key driver for the industry is the existence of low NO<sub>x</sub> burners where NO<sub>x</sub> emissions are <25 ppm or ultra-low NO<sub>x</sub> burners (< 10 ppm). The nozzles in these burner designs can foul very quickly with carbon deposits. This leads to poor furnace efficiency and could even damage the convection sections of the furnace<sup>4</sup>.

Fuel gas is often used to regenerate molecular sieve beds (dehydrators), and then is routed to the furnace as fuel. During regeneration at 200-230°C, the gas strips out the formed and deposited oils from the molecular sieves, and so the fuel gas thus becomes contaminated with these oils. This contaminated fuel gas then causes fouling of the furnaces' burners, and thus more frequent and costly burner tip cleaning. Fouling of low NO<sub>x</sub> burner nozzles also leads to lower NO<sub>x</sub> removal efficiency.

There are several sources of these oils, including green oil if the sieve bed is downstream of an acetylene hydrogenation unit, and carryover of compressor lube oils. Oils may also be produced if the regeneration gas contains low level of reactive hydrocarbons. For instance, an ethylene plant's offgas used as regeneration gas may contain nominally 1% ethylene. These hydrocarbon liquids crack when they encounter the hot surface of the tip, leaving behind coke on the surface.

Besides these oils, fuel gas may have particulates such as line scale, salts, dirt and molecular sieve fines (due to abrasion) that also contribute to burner tip plugging. Plugged tips must be cleaned quickly before more serious maintenance problems develop, such as flame instability.

Green oil is a mixture of C<sub>4</sub> to C<sub>20</sub> unsaturated components and cannot be avoided. It is formed in all the C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> hydrogenation reactors. In the two stage acetylene hydrogenation reactor with Palladium on Alumina catalyst, the acetylene is hydrogenated to ethylene and ethane. Green oil is formed in the side reactions. The low molecular weight fraction of the green oil vaporizes into the gas stream. Portions of the heavier fraction deposit on the pores of the catalyst. Much of the heavier fraction goes into the gas stream and is present in the 100-1000 ppm concentration range and is present as fine droplets<sup>5</sup>. It also deposits on the material of the molecular sieve driers – alumina/zeolites. When the molecular sieve beds are regenerated with hot gas around 200°C, the green oil escapes into this gas and ultimately polymerizes on the burner tips. Green oil has harmful effects not only on the burner tips but also on the ethylene fractionator (C<sub>2</sub> splitter tower). Back-end hydrogenation process creates increased amounts of green oil compared to the front end hydrogenation process.

Several industrial methods<sup>5</sup> for the separation of green oil from the hydrogenation reactor gaseous effluent stream have been considered including:

- Washing of the wet gas stream from the reactor with a liquid ethylene stream in a stripping tower
- Impaction of the wet gas through a packed bed
- Separation by a mesh pad in a knock-out drum
- Use of a high-efficiency liquid-gas coalescer with specially formulated and designed filter media

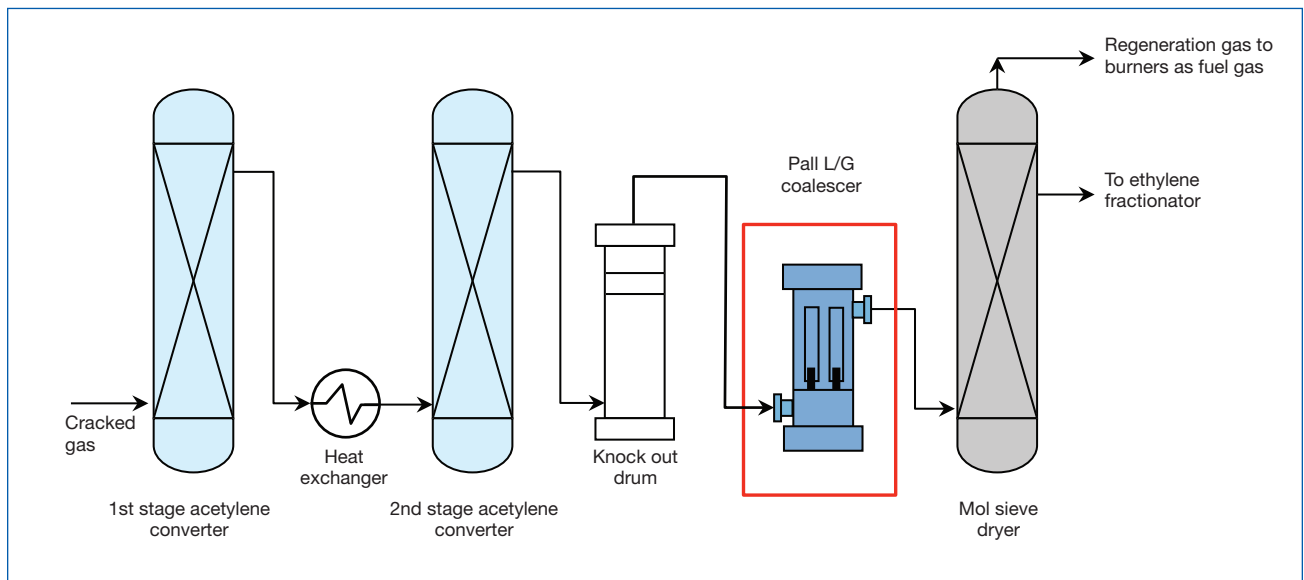
Of the separation options investigated, the high-efficiency liquid/gas coalescer was found to be the most cost effective option.

### Mitigation

The principal economic drivers for the plants include:

- Increase period between molecular sieve regeneration and thereby reduce the operating costs/maintenance costs and increase life of bed material
- Burner tip protection
- Mitigating fouling reactions in ethylene fractionators and extending its run length

Highly efficient liquid/gas coalescers have been used to capture green oil as shown in **Figure 5**.



**Figure 5:** Schematic Showing Use of a Liquid/Gas Coalescer to Mitigate Green Oil

### Case Study 5

A major U.S. Gulf Coast ethylene plant was experiencing green oil related fouling in their back end acetylene converters. Gas chromatography analysis confirmed that the green oil content was in the range of 25-50 ppm.

There were three main objectives:

1. Protect burner tips in the furnaces from green oil fouling. The regenerated methane gas from the molecular sieve bed was being sent to the burners as fuel gas
2. Eliminate the green oil fouling problem in the feed to the molecular sieve bed and ethylene fractionator
3. Provide protection to interstage hydrogenation reactors.

A pilot liquid/gas coalescer test unit successfully took 25-50 ppm of green oil down to below the detection limit (< 1 ppm). The full scale commercial coalescer has performed satisfactorily with element replacements at intervals of one year or more.

### Case Study 6

A European ethylene producer<sup>6</sup> experienced clogged furnace burner nozzles. An extensive investigation revealed that a compressor was losing 20 liters of lube oil/week. It was treating a small amount of methane from the cold box and increasing pressure to the fuel gas pressure. This oil in fuel gas was being transported to the burners. Further, dust from the molecular sieve driers and catalyst fines were also found upon analysis of the deposits in the burner tips.

The solution was the installation of a high-efficiency liquid/gas coalescer to protect the burner tip nozzles. It reduced the contaminant level to undetectable in the product gas. The surface treated elements worked well and are being replaced once a year.

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