



Improve Steam Cracking Furnace Productivity and Emissions Control through Filtration and Coalescence

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The impact of feedstocks on the operation of an ethylene plant April 26, 2006

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Abstract

Hydrocarbon streams feeding ethylene steam cracking furnaces often contain significant levels of corrosion products, water, and salts. This is especially true when naphtha is supplied by marine vessels. In these cases, high efficiency liquid-liquid coalescers and filters are recommended to condition the inlet feed stream.

Contaminants in the inlet hydrocarbons can adversely affect ethylene production in a number of ways. Sodium and iron oxides are known to be coke promoters, and their presence can reduce the run time of the ethylene furnaces before decoking is required, and in some instances reduce the life of the furnace tubes by as much as one third. Unscheduled or frequent decoking cycles lead to a loss in ethylene production, shortened furnace tube life, and create higher maintenance costs. Frequent decoking will also result in increased particulate release to the atmosphere and can create environmental concerns over excessive emissions. Fouling of flow meters and control valves can lead to diffi-

culty in maintaining the optimum furnace temperature and steam/hydrocarbon feed ratio. This can lead to poor yield of ethylene by the cracker and undesirable by-products.

Installation experience at The Dow Chemical Company (Dow) in Freeport, Texas is presented for the use of high efficiency liquid-liquid coalescers and filters to extend the steam cracker service life between decokings. The naphtha feed was supplied by marine transport and contained significant salt water contamination. An economic evaluation of the savings due to improved operation efficiency and the payback period for the coalescer system is provided. The installation of the high efficiency coalescer-filtration system was found to have a payback of less than ten months based on extended furnace run times alone, assuming that ethylene production is limited by furnace availability.

Introduction

Rising costs for raw materials and ever-increasing competition have made margins in ethylene production slim in recent years. Many producers are looking for ways to reduce costs, including using alternate feed stock supplies such as those shipped in by marine vessels, or the use of Light Catalytic Cracked Naphtha (LCN) or Fluidized Catalytic Cracked (FCC) gasoline.

While alternate steam cracker feed stock sources can reduce raw material costs, they also pose new challenges to ethylene producers. Contamination in the feed stocks can include corrosion products, water, and salts. Marine transport vessels may also use the same tanks for seawater ballast as they use for hydrocarbon feed stocks, thus creating a greater risk of contamination to steam cracker furnaces.

The cracking of LCN or FCC gasoline is a recent trend, due to the new 2005 specifications on refining products. While all feed stocks can bring solids due to pipe corrosion, LCN or FCC gasoline has additional sodium contamination due to previous treatment to remove sulfur compounds. The desulfurization process includes a caustic wash step that results in high sodium concentrations that should be removed prior to the furnaces.

Contaminants in the inlet hydrocarbons can adversely affect ethylene production in a number of ways:

- Sodium and iron oxides are known to be coke promoters [1,2] and their presence can reduce the run time of the ethylene furnaces before decoking is required. Unscheduled or frequent decoking cycles can lead to a loss in ethylene production, shortened furnace tube life, and higher maintenance costs.
- Fouling of flow meters and control valves can lead to difficulty in maintaining the optimum furnace temperature and steam/hydrocarbon feed ratio. This can result in a poor yield of ethylene by the cracker and undesirable byproducts.
- Coke fines and sodium are often released inadvertently into the downstream quench systems during decoking cycles and this can lead to further complications in the decanter and downstream separation units, including the quench water stripping tower and heat exchangers in the dilution steam system.

- During decoking cycles, significant amounts of particles are released to the atmosphere: The total annual emissions can be reduced as the number of cycles is decreased.

Separation of the harmful contaminants can be a difficult task especially when the salt water is emulsified with the hydrocarbon feed stock. Fortunately, new liquid-liquid coalescer technology has been developed to separate even the most difficult emulsions.

Experience with high efficiency liquid-liquid coalescers and filters at The Dow Chemical Company (Dow) in Freeport, Texas is presented. The naphtha feed is marine transported, and both sodium and iron needed to be removed prior to the cracking furnaces. Details of the filtering and coalescing systems are provided along with the separation performance, process benefits, and payback period.

Solid and Salt Water Contamination in Naphtha Streams

Solid contamination

Solid contamination in naphtha

A recent study based on 36 samples of naphtha cuts from 19 refineries worldwide (11 different oil companies) showed that the quantity of solids in naphtha varied between 1 and 10 ppmw. The particles were composed of iron oxides and iron sulfides with a size range between 2 and 70 micron (μm) and an average size of 10 μm [3]. Depending on the naphtha cuts (catalytic cracked naphtha, naphtha straight run as examples), the particle content may be significantly different. Filters have already been successfully installed for the protection of naphtha hydrotreaters in refineries.

Analysis of solid contamination in naphtha performed on steam crackers

Analysis of different naphtha feeds was performed on crackers prior to the furnaces and are consistent with the study on refineries:

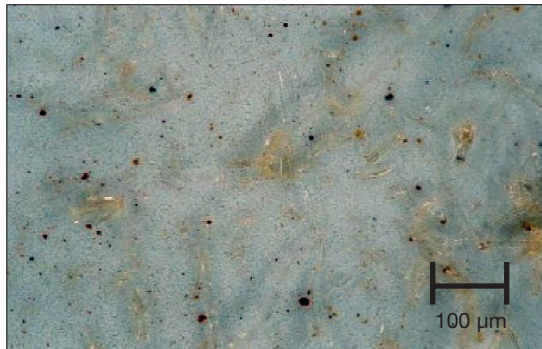
Table 1: Naphtha solid contamination: measurements of TSS* on naphtha crackers

Location	TSS value
USA plant 1	1.2 to 1.5 mg/l
USA plant 2	4 to 6 mg/l
Japan	1.3 mg/l
Average	3 mg/l

* Total Suspended Solids

A photomicrograph of typical solid contaminants in naphtha is presented in Figure 1. The red-orange colors are indicative of iron oxides while the black particles are representative of coke fines and iron sulfides.

Figure 1:
Photomicrograph
of naphtha solid
contaminants at
100 X
magnification



Based on the analysis of thirty six different naphtha streams, it can be stated that the typical solid contamination in naphtha is in the range of 1 to 10 ppmw in crackers and refineries. Iron oxides and iron sulfides represent the main part of the solid contamination with more than 80% of the particles having sizes below 70 μm , and an average size of 10 μm .

The naphtha filter rating: finding the best compromise to optimize furnace protection

Typically, large solid particles (>300 μm) are removed in the storage tanks or by coarse mesh filters installed upstream of the furnaces. However, for efficient protection of furnace tubes, the removal ratings of the naphtha filters should be lower than 70 μm absolute. Considering absolute filter efficiencies, and the particle size distribution in the naphtha, a 10 μm absolute rating is recommended. Since 1998, the plants having such filter installations have reached the expectations in terms of furnace protection and cost operation.

Emulsified water

Laboratory tests determined that the interfacial tension between water and naphtha at the cracking plants and in refineries ranged from 1 to 24 dyne/cm. An interfacial tension below

20 dyne/cm indicates that the emulsion is very stable. Under such conditions, separation in storage tanks is ineffective except for bulk water removal, and a small percentage of emulsified water would be expected to remain in a stable form, requiring the use of high efficiency liquid-liquid coalescers for separation.

Depending on variations in process operations, interfacial tensions can vary dramatically. At the refinery where naphtha is produced, corrosion inhibitors (filming amine type) are typically injected into the overhead column to minimize corrosion in the separation drum and overhead heat exchangers. Variations in inhibitor content can significantly affect emulsion stability of water in naphtha.

High Solids Loading Naphtha Filter: Naphtha feed stocks can contain significant solid particulate in the form of corrosion products (iron oxides, iron sulfides), and in lower quantities silt (sand, clay) or precipitated salts (sodium chloride, sodium sulfate, etc.). In some cases, aqueous contaminants are not present, and in others, both aqueous and solid contaminants need to be removed. Therefore, in some instances, the feed stock may require stand-alone particulate filtration, and in others cases, incorporate a coalescer system with pre-filters.

In order to protect the steam cracker, a filter with an absolute rating of 10 μm should be used. Several types of filters are available, including string wound, pleated, depth, and advanced high flow capacity designs that use laid over, crescent-shaped pleats. When the solids loading is high, backwash type filters become more economical than disposable type. Here, the initial capital investment is higher, but the operating costs are much lower since the filters are regenerable and can last years before requiring cleaning. An example of a high flow capacity horizontal disposable filter system is shown in Figure 2:

Figure 2:
High flow capacity
pre-filter offering
high surface area.



High Efficiency Liquid-Liquid Coalescers:

The separation of emulsified water in the feed hydrocarbon to the steam cracker can be a difficult proposition. Settling tanks, vane separators, and mesh pads will not break emulsions and can allow harmful contaminants to pass through. Traditional liquid-liquid coalescers use glass fiber media and are adequate for easy to separate emulsions with interfacial tensions greater than 20 dyne/cm, but will not work for more difficult emulsions. At interfacial tensions below 20 dyne/cm, surfactants adsorb onto glass fiber media, rendering them ineffective at coalescing. This phenomenon is known as “disarming.”

Pall Corporation has developed and patented new non-disarming coalescer media that is constructed with novel, formulated polymers and fluoropolymers. These high efficiency coalescers are effective for emulsions having interfacial tensions as low as 0.5 dyne/cm [4] and have been used for difficult separations, including water-methanol from LPG [5] and caustic from gasoline [6]. Naphtha feed stocks at an ethylene plant in the Benelux were found to have interfacial tensions with water as low as 1 dyne/cm [7]. High efficiency, polymeric coalescers have produced clean petroleum fuels with free water concentrations of <15 ppmv when challenged with inlet dispersed concentrations of up to 10%. The typical life of the coalescers is greater than one year and the pre-filters generally last several months, making the use of high efficiency liquid-liquid coalescers economical.

High efficiency liquid-liquid coalescers merge small droplets of the aqueous phase liquid into larger ones as the fluid stream passes through several layers of filter media, each with progressively larger pores. As droplets compete for open pores, they coalesce to form larger droplets. The larg-

er droplets are easier to separate from the continuous hydrocarbon phase liquid. The enlarged coalesced drops are then removed from the hydrocarbon phase by a separator cartridge that repels the water drops but allows the hydrocarbon to flow through. An illustration of the vertical high efficiency liquid-liquid coalescer system is given below in Figure 3:

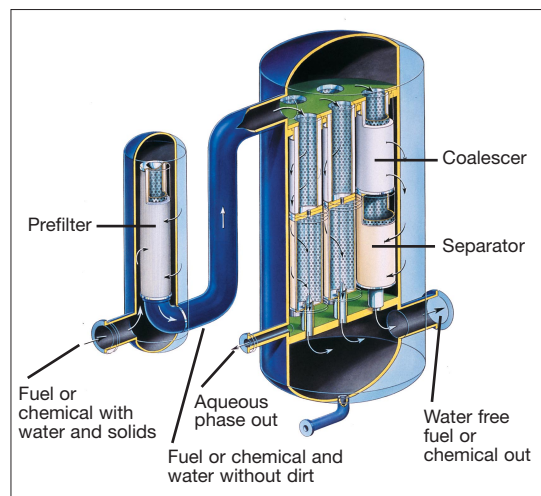


Figure 3:
High efficiency coalescer system with coalescer
elements stacked on top of separator elements.

The high efficiency liquid-liquid coalescer operates in three stages: 1) separation of solids; 2) coalescence; and 3) separation of coalesced drops.

Separation of Solids: Suspended solids can increase the stability of an emulsion and reduce the effective life of the coalescer. Effective pre-filtration to remove these solids is an important consideration for a coalescer system. Types of filter systems are discussed in a previous section, “High Solids Loading Naphtha Filter.”

Coalescence: In this stage the pore dimensions are very fine at the beginning and become more open to allow void space for coalescing droplets. The inlet dispersion containing fine droplets between 0.2 to 50 μm is transformed into a suspension of enlarged drops ranging from 500 to 5,000 μm . The coalescence mechanism involves adsorption of droplets onto the coalescer fibers, followed by translation along the fibers and collisions at the junctures between fibers. In these collisions, the droplets merge together, or coalesce. The viscous drag of the bulk fluid stream then causes the

enlarged drops to disengage from the fibers. This process is repeated a number of times through the coalescer depth until the large, coalesced drops exit the coalescer media [4].

Separation of Coalesced Drops: Once the droplets have coalesced, separation is achieved by using a separator cartridge that deploys a hydrophobic medium. The separator repels the aqueous phase

drops, so only the water-free bulk hydrocarbon fluid passes through the separator. In Pall Corporation's design, the coalescer is stacked on top of the separator. This design ensures evenly distributed flow to the separator and enhances performance. The aqueous phase collects in an internal sump. A level control system is used to drain out the collected aqueous phase and maintain the hydrocarbon level.

Plant Experience

Plant experience at The Dow Chemical Company's, Freeport, Texas site is described below. Included are operating data and plant benefits resulting from the use of high efficiency liquid-liquid coalescers and filters on the feed naphtha.

Process Parameters

The process conditions for naphtha feed are given below in Table 2:

Table 2: Process conditions of naphtha feed to steam crackers

Pressure	200 psig
Temperature	80°F
Viscosity	0.41 cP
Inlet Water Concentration	1 – 2%
Sodium Content in Water	13,000 ppmw
Magnesium Content in Water	1,300 ppmw
Total Inlet Sodium Content	130 – 260 ppmw

Filter and Coalescer Systems Operation Experience

The high efficiency coalescer unit was installed in January 2004. This system consisted of 104 high efficiency AquaSep® polymeric liquid-liquid coalescers with 104 stacked separator cartridges (both 20 inch length by 4 inch diameter) to treat a maximum design naphtha flow. A separate filter system consisting of 36 Ultipleat® high flow glass fiber filters with an advanced laid over, crescent shaped design (60 inches length by 6 inch diameter and 2 micron absolute rating) was used to protect the coalescers.

After start up, the naphtha was found to contain higher solids than originally expected and this led to prefilter service life of less than two weeks. The coalescer, however, was effective in removing large volumes of water and lowering the sodium content in the outlet naphtha as evidenced

by increased steam cracker run times. High efficiency liquid-liquid coalescers on similar naphtha streams in ethylene plants have been found to reduce the sodium content down to < 0.2 ppm Sodium [7].

In order to optimize the coalescer-filter system operation, a twofold approach was adopted. Alternate coalescers and filters were selected that were capable of processing higher solids loading and a process change was also undertaken.

Coalescer– Filter optimization: The AquaSep coalescers were replaced with PhaseSep® coalescers that are designed with a fluoropolymer construction and are able to process higher solids compared to the AquaSep coalescer design. The pre-filter grade was changed from the original two micron absolute to a coarser ten micron absolute.

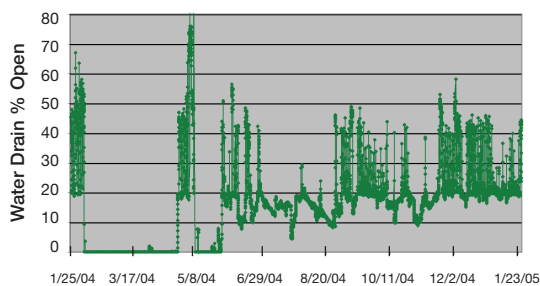
Process Optimization: Originally the naphtha was fed directly to the coalescer-filter system by a pipeline connected to the unloading marine transport. A holding tank was installed on shore subsequently, and this allowed for settling of the larger particulate and reduced the load to the coalescer-filter system. The feed source was changed from the pipeline to the shore tank in July 2004.

These changes optimized the system and allowed for economical prefilter service life of over two months while protecting the coalescers from solids fouling. The PhaseSep coalescer system has experienced a coalescer element service life of over a year and has consistently removed large volumes of salt water reducing the harmful sodium content that was being fed to the steam cracker. The operation of these systems has met or exceeded the design requirements in terms of service life and performance regarding furnace protection.

Operation Data

The operating data for the coalescer-filter system at Dow is presented for the period of January 2004 to January 2005 for water drain operation, coalescer differential pressure, pre-filter differential pressure and the system naphtha feed flow rate. In Figure 4, the data collected for the water drain operation is given. Water is collected in the coalescer sump and accumulates. An automatic drain is opened at different intervals triggered by an upper limit sensor. Per the instrumentation settings, water will drain only after the water drain % open value reaches 20%. During the period between February–April in 2004, the sensor collecting the data was not online, explaining why the graph indicates a zero reading for this period. The data over the year's operation shows repeated valve opening indicating that the coalescer was effective in removing salt water contamination.

Figure 4:
Water Collection by
the High Efficiency
Coalescer System



In Figure 5, the data on the coalescer differential pressure is presented. Initially, the AquaSep coalescers were installed and the feed was directly from the ship pipeline. The naphtha stream contained higher than expected solids and this led to short coalescer life, which is illustrated by a rapid rise in the differential pressure in early February 2004 that was over 20 psid and off the scale in Figure 5.

The coalescers were then changed to the PhaseSep coalescer, which is less sensitive to solids loading. The feed was also changed from the direct pipeline to an onshore settling tank in July, 2004. Over the course of the rest of the year's operation, the coalescer differential pressure increased gradually up to a maximum of

4 psid. The coalescer can operate effectively up to 15 psid and the typical service life for these coalescers is 2 years. The data indicated in Figure 5 show that the coalescer is operating within design specification and has plenty of service life remaining.

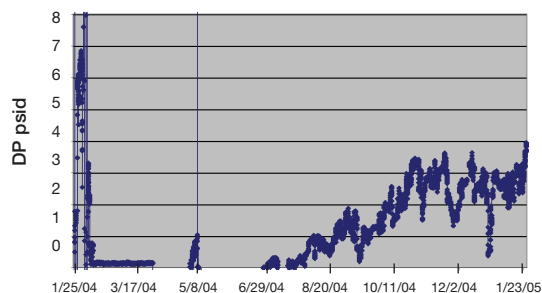


Figure 5:
Coalescer Differential Pressure

The information regarding the prefilter differential pressure is presented in Figure 6. The pre-filters are changed out after the differential pressure reaches 20 psid, which is well below their burst strength rating. The prefilter life was initially shorter than expected and averaged about 2 weeks. Data was not being collected between February–March 2004 and the graph indicates no readings during this period.

The changes in the type of pre-filter and coalescer as well as the use of a settling tank located onshore were implemented by July 2004. After these changes were made, the service life of the pre-filters increased to about 2 months as indicated by Figure 6.

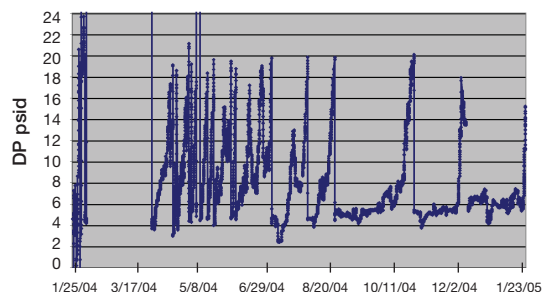


Figure 6:
Prefilter Differential Pressure

The naphtha flow rate can have a major impact on the coalescer and prefilter performance, and so this data is included in Figure 7. For the most part, the naphtha flow rate averaged between 60–67% of the rated design flow rate from May 2004 until January 2005. The flow rate had dropped down to below 30% in March–April, 2004 and the initial flow rate in January–February, 2004 was a bit higher at around 60–80% of the rated design. The operating flow rates have been below the rated design (100%) and the coalescer has performed effectively throughout this period. Due to the mechanisms of diffusive capture and direct interception, the coalescer performance is not affected by turndowns in the flow rate. While not all of the data was being recorded dur-

ing the lowered flow rate period, the coalescer did show frequent water drain valve opening in April 2004 when the naphtha flow rate was decreased.

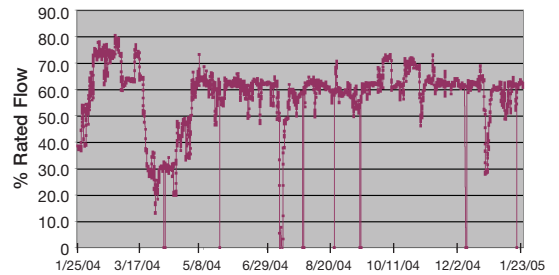


Figure 7:
Naphtha Flow Rate

Process Benefits

The primary benefit to the ethylene plant operation as a result of upgrading the fluid conditioning of the feed naphtha was to extend the run length of the furnaces due to reduced coking. The furnace run lengths increased an average of 33%. This led to a savings of \$2.0 million dollars per year due to the coalescer installation.

The total capital plus installed cost of the coalescer and filtration system was estimated at \$1.5 million dollars (with installation cost at 3-5 times the capital cost). The annual operating cost was calculated to be less than 10% of the capital plus installed cost of the system based on the coalescers lasting 2 years and the prefilters lasting 2 months. Using these calculations the payback period due to furnace run time improvements alone is estimated at less than ten months assuming that ethylene production is limited due to furnace availability.

The coalescer system also provided the following additional process benefits for Dow:

- Reduced fouling and plugging in the cracking coils
- Lowered fuel gas consumption due to less fouling
- Improved control of the naphtha to steam ratio due to reduced fouling of control valves and flow meters
- Reduced maintenance costs associated with mechanical cleaning of the transfer line exchangers
- Lengthened furnace tube life due to the use of liquid-liquid coalescers, which helped eliminate the sodium attacks that drastically reduce the lifespan of the tubes
- Reduced CO formation and concentration in the cracked gas
- Lowered particle and CO₂ emissions due to less decoking operations in one year.

Conclusions

High efficiency liquid-liquid coalescers and filters used to treat liquid or gas hydrocarbon feeds in ethylene plants were found to increase the steam cracker productivity and lower emissions by decreasing the decoking frequency. In crackers fed with barged naphtha, the newly developed liquid-liquid coalescers removed fouling and coke-generating contaminants including sodium. Filters and coalescers successfully protected the furnaces at Dow in Freeport, Texas.

Major benefits of using high efficiency liquid-liquid coalescers and filters include the reduction of fouling in the cracking coils, the extension of the run length of the furnaces

between de-coking, increasing the useful life of the furnace tubes, and the lowering of emissions. This technology also enables ethylene plants to use more contaminated, alternate feed stocks such as naphtha brought in by marine transport or Light Cat-cracked Naphtha (LCN/FCC gasoline) coming from refineries. The payback period for the capital investment in the high efficiency coalescer and pre-filter systems was estimated to be less than ten months assuming that ethylene production is limited due to furnace availability. The operating costs were found to be reasonable at less than 10% of the capital and installed cost of the coalescer-filter system.

References

1. Orriss, R., "Effects of Contaminants in Ethylene Plants: Sodium and Iron," AIChE Conference, Spring Meeting, 1996.
2. Albright, L.F., "Ethylene Tubes Studies," Oil & Gas Journal, Aug. 1-1988, Aug. 15-1988, August 1988.
3. Darde, T., "Feed Filtering Requirements," Axens Prime G+ customer seminar; November 2002.
4. Brown, R. L., Wines, T. H., "Difficult Liquid-Liquid Separations," Chemical Engineering; December 1997, Vol. 72, No. 12, p. 95.
5. Hampton, P., Darde, T., James, R.H., Wines, T. H., "Liquid-Liquid Separation Technology Improves IFPEXOL Process Economics," Oil & Gas Journal; April 2001.
6. Katona, A., Darde, T., Wines, T. H., "Improve Haze Removal for FCC Gasoline," Hydrocarbon Processing, August 2001, Vol.80, No.8, pp. 103-108.
7. Balouet, S., Wines, T. H., and Darde, T. "Contribution of Filtration and Coalescence to Steam Cracking Furnace Productivity and Emissions Control," European Ethylene Producers Conference, Vienna, Austria, October 2004.



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