

PETROCHEMICAL DEVELOPMENTS

Improve contaminant control in ethylene production

New separation methods effectively remove aerosols and particulates that compromise heat-transfer surfaces

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Managing contaminants in ethylene production is critical. Contaminants in processing streams can compromise production efforts, foul major equipment operations such as heat exchangers, compressors, etc., and cause unscheduled shutdowns. Many processing streams within the ethylene unit are inter-related; thus, removing contaminants early within the process can reduce fouling-related issues in downstream process units.

Filtration and phase separation methods can be applied in various locations in ethylene units to provide benefits. Potential contaminant removal applications include: feedstock treatment, quench water, caustic treating, acetylene converters and fuel-gas systems. Using contaminant mitigation efforts can extend the service life of the steam cracker, reduce fouling in benzene strippers and heat exchangers, lengthen cycles between regeneration in molecular sieve dryers and improve operation of low NO_x burners.

Advances in filtration and coalescer technology have been successfully applied in ethylene plants. The examples presented demonstrate potential benefits available through separator and coalescer technologies.

SEPARATION TECHNOLOGIES

Separation methods for ethylene production involve a variety of options. Possible solutions include:

Liquid/liquid coalescers. High-efficiency liquid-liquid (L/L) coalescer systems can process inlet discontinuous phase concentrations up to 10% and reduce them to ppm levels in the outlet. These units can effectively treat difficult-to-separate emulsions with interfacial tensions as low as 0.5 dyne/cm. Using polymers and fluoropolymers in the construction of the coalescer materials allows expanded applications over earlier conventional types. The new materials do not disarm in the presence of surfactants and can withstand an array of aggressive chemical applications over a wide range of temperatures from -40°F (-40°C) up to 300°F (149°C).¹ When properly protected by pre-filters, L/L coalescers can have service lives of 1–2 years. The L/L coalescing system operates in three stages:

- Separation of solids/pre-conditioning
- Coalescence
- Separation of coalesced drops.

Separation of solids/pre-conditioning. Solids can increase the stability of an emulsion; removing solids can make coalescing easier. Generally, this step can be achieved by a separate car-

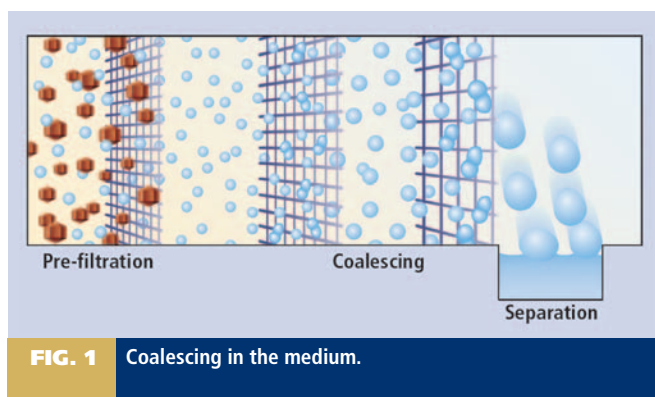


FIG. 1 Coalescing in the medium.

tridge-filter system or by a re-generable backwash filter system for high solids levels. In addition, the filtration stage protects the coalescer and increases service life. This step also initiates the coalescing of the hydrocarbon droplets, thereby enhancing separation capabilities.

Coalescence. In the coalescence stage, pore dimensions begin with a very fine structure and then become more open with void space for the coalescing droplets. In the primary coalescence zone, the inlet dispersion containing fine droplets, in the size range of 0.2–50 microns is transformed into a suspension of enlarged droplets of 500–5,000 microns. The specific surface properties of the coalescer fibers are critical and influence the adsorption of droplets as well as the ultimate release after coalescing. If the affinity of the droplets to the fibers is high, the capture efficiency is increased. Yet, if the affinity is too great, the adverse effect of reducing the droplet disengagement efficiency can occur. This can create drops that are less than the maximum size exiting the coalescer medium.

Separation of coalesced droplets. Once the droplets have been coalesced, they are now as large as possible for the given flow conditions. Separation can be achieved in either a horizontal vessel where the coalescer is followed by a settling/drop disengagement zone or by a vertical two-stage system where the coalescer stage is followed by a separator cartridge.

The horizontal configuration (Fig. 2) is recommended for separating hydrocarbon contaminants from water or removing aqueous contaminants from hydrocarbons when the interfacial tension is very low (< 3 dyne/cm).

The vertical configuration (Fig. 3) is recommended for removing water or aqueous contaminants from hydrocarbon streams when the interfacial tension is > 3 dyne/cm. The separation stage is achieved

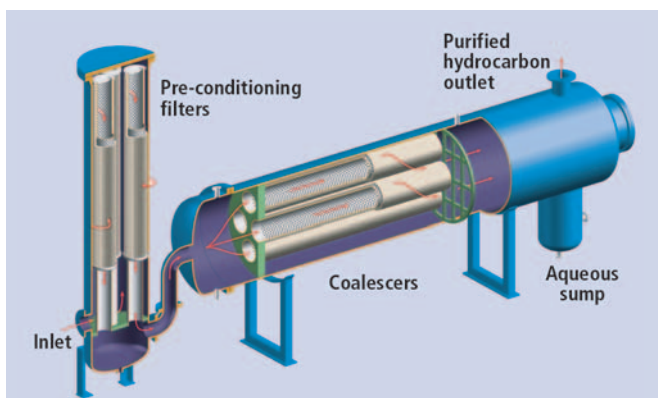


FIG. 2 Cross-sectional view of horizontal liquid-liquid coalescer.

with hydrophobic-separator cartridges. This system provides an effective barrier to aqueous coalesced drops, but allows hydrocarbon to pass through them. The separator cartridges can be stacked below the coalescers for optimum utilization of the separator medium.

Particulate filters. Removing solid particulate from liquid streams can be achieved by disposable filters and regenerable or continuous use filters. Disposable filters are generally used when the solids content is less than 10 ppm and the service life can vary from a few weeks to a few months. They are available in a variety of configurations, including string wound, pleated, melt-blown depth, bag and advanced crescent-shaped pleats. Materials of construction can include cotton, cellulose, glass fiber, polypropylene, nylon, polyphenylene sulfide and other polymeric materials. Regenerable filter systems are recommended for higher solids contents. They have a higher initial capital cost but will not require change-out of disposable elements. Regenerable filters are typically constructed from stainless steel for durability.

Liquid/gas coalescer technology. High-efficiency liquid/gas (L/G) coalescers can remove liquid aerosols from gas streams. They are capable of removing very fine drops in the sub-micron range that often originate from condensation. These coalescers separate aerosols based on a diffusion mechanism, which provides excellent efficiency even at flowrates well below design conditions. Other technologies, including cyclones, demister pads and vane separators, are not efficient at separating small aerosols. They lose efficiency at reduced flowrates since they operate on an inertial-based separation mechanism.

L/G coalescers are generally constructed from glass fibers since this material allows for a fine porous structure with fiber diameters of a few microns. Using a fluorocarbon surface treatment can greatly enhance separation performance and reduce the size of the L/G coalescers.² High-efficiency L/G coalescers are used for inlet aerosol concentrations of up to 1,000 ppmwt (0.1 %) and provide outlet concentrations as low as 0.003 ppmw.^{3,4} A schematic of a high-efficiency L/G coalescer is shown in Fig. 4.

Oil purifier. Purifying lubricating oils for gas compressors and other rotating equipment is critical when maintaining optimized operation. Water, solid particulate and even gases can accumulate in the lube oil and cause detrimental effects. Excess contaminants can lead to unplanned shutdowns, high maintenance

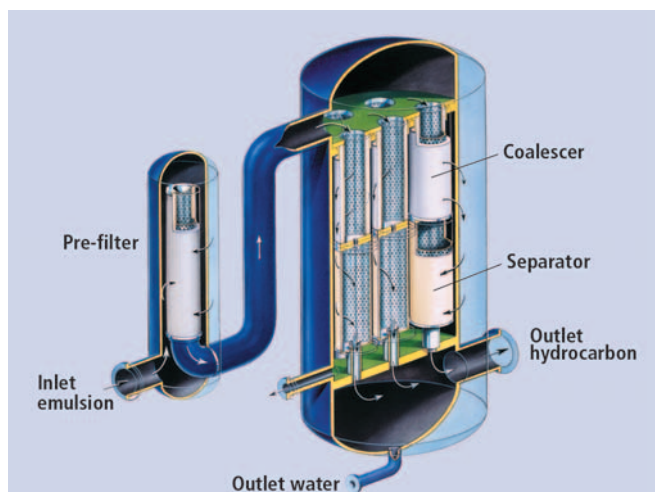


FIG. 3 Cross-sectional view of vertical liquid-liquid coalescer.

costs and, in some cases, catastrophic failure of compressors requiring replacement of expensive components. An oil purifier is a cost-effective way to reduce the risk with lube-oil issues. The oil purifier uses a two-stage process in which free and dissolved water and gases are removed through a vacuum-dehydration step utilizing spinning disks to maximize mass transfer. Following the vacuum dehydration step, an absolute-rated particulate filter removes solid contaminants down to less than one micron.

Separations options in an ethylene plant. A general schematic of a liquid cracker and back-end acetylene converter is shown in Fig. 5. The locations for various filter/coalescer sites are noted on Fig. 5. Table 1 summarizes the location, type of separation equipment and process benefit attainable.

Feedstocks. Rising costs for raw materials and ever-increasing competition have narrowed margins in ethylene production. Many producers seek options to reduce costs. Options include using alternate feedstock supplies such as those shipped in by marine vessels or using light catalytic naphtha (LCN) or fluidized catalytic cracked (FCC) gasoline.

While alternate steam cracker feedstock sources can reduce raw material costs, they also introduce new challenges. Contaminants found in the feedstocks include corrosion products, water and salts. Marine transport vessels may also use the same tanks for seawater ballast as for carrying hydrocarbon feeds, thus creating an even greater risk of contamination to steam cracker furnaces.

Sodium and iron oxides are known coke promoters. Their presence can reduce the run time of 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 cause difficulty in maintaining the optimum furnace temperature and steam/hydrocarbon feed ratio. Poor control results in poor ethylene yield and generates undesirable byproducts. Coke fines and sodium are often released inadvertently into the downstream quench systems during decoking cycles. The fines and salts contribute to further complications in the decanter and downstream separation units, including the quench water stripping tower and heat exchangers in the dilution-steam system.

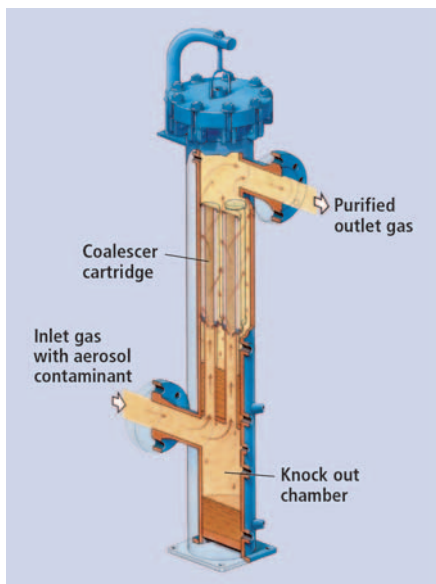


FIG. 4 Flow pattern of a liquid-gas coalescer.

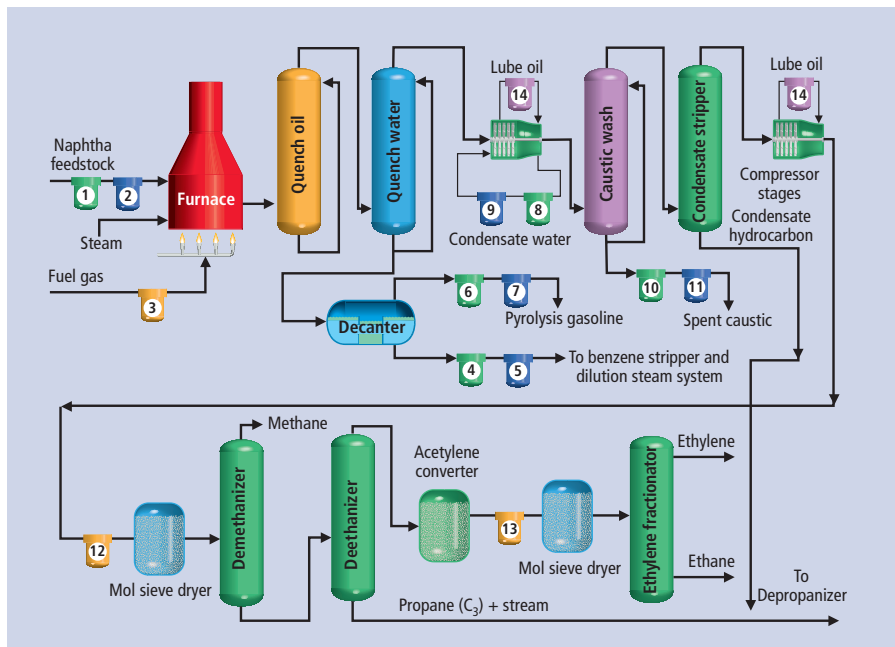


FIG. 5 Ethylene plant with liquid cracker and back-end acetylene converter.

Upgrading the fluid conditioning of the ethylene feedstocks provided many benefits at commercial plants located in Benelux, Germany, China and Australia.⁵ In some cases, other non-filtration related process improvements were made; yet, installing high-efficiency filters and/or high-efficiency L/L coalescers was an important part of the total plant optimization. Several processing benefits were realized through separation technologies:

- Extended run length of the furnaces from 25% to 33% due to reduced coking
- Reduced fouling and plugging in the convection zone, better

heat flux in the convection section and 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 flowmeters
- Reduced maintenance costs associated with physically cleaning the steam crackers during decoking
- 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.

TABLE 1. Filtration and separation options with an ethylene unit

Filter number	Process application	Separation type	Process benefit
1	Naphtha feed to steam cracker	Solid from liquid	Extend furnace run time
2	Naphtha feed to steam cracker	Liquid from liquid	Extend furnace run time
3	Fuel gas	Liquid and solid from gas	Prevent burner fouling
4	Quench water	Solid from liquid	Protect benzene stripper
5	Quench water	Liquid from liquid	Protect benzene stripper
6	Pyrolysis gasoline	Solid from liquid	Protect hydrogenation catalyst
7	Pyrolysis gasoline	Liquid from liquid	Protect hydrogenation catalyst
8	Compressor condensate	Solid from liquid	Re-inject condensate water to compressor
9	Compressor condensate	Liquid from liquid	Re-inject condensate water to compressor
10	Caustic treating	Solid from liquid	Remove red oil from spent caustic
11	Caustic treating	Liquid from liquid	Remove red oil from spent caustic
12	Cracked gas upstream of de-methanizer	Liquid and solid from gas	Protect mole sieve dryer
13	Cracked gas after acetylene converter	Liquid and solid from gas	Protect mole sieve dryer
14	Cracked gas compression—lube oil	Solid, liquid and gas from liquid	Protect compressor

Quench water. The pyrolysis reaction to form ethylene from naphtha feeds produces a liquid hydrocarbon byproduct known as pyrolysis gasoline (py-gas). Py-gas is composed of a mixture of light hydrocarbons including benzene, toluene, xylene, styrene, ethylbenzene, naphthenes, and C₅–C₁₀ unsaturated, linear, iso and cyclic hydrocarbons. In addition, py-gas is reactive and will polymerize to form sticky gums and higher molecular weight polymers that can foul process equipment. Heavy oil originating from the oil-quench tower can also be present from carryover into the quench water along with the py-gas. Quench water and py-gas mixture readily form stable emulsions. The stability of these emulsions is due to the surfactant properties of the py-gas components, which will vary depending on the feedstocks cracked to make ethylene and chemical additives used.

Quench water leaving the quench tower is split into a recycle stream that returns to

the quench tower through a cooling loop and a dilution steam system (DSS). Excess water is sent to a wastewater treatment facility. To re-use the quench water for steam production, the water must be processed to remove contaminant hydrocarbons (quench oil, pyrolysis gasoline) or other contaminants that can foul heat exchangers and boilers, lead to poor separation in stripping units, increasing energy consumption. The quench water is treated by a decanter (gravity separation) that can operate alone or in conjunction with a coalescer system before being processed through heat exchangers and a stripper column (benzene stripper) to remove dissolved hydrocarbons. The treated quench water is sent to the dilution steam system (DSS), which includes the boilers for generating steam.

Commercial experience at ethylene plants located in the US, Europe and Asia has proven the effectiveness of using L/L coalescers for this application.⁶ Process benefits included:

- Extended service life of the steam stripper between cleanings
- Reduced fouling and maintenance of heat exchangers
- Lowered steam usage
- Higher recovery of pyrolysis gasoline
- Less unscheduled plant shutdowns.

Acetylene converter—green oil. Acetylene is difficult to separate from the ethylene cracked-gas stream due to its similar volatility. Typically, acetylene is converted to olefins by selective hydrogenation or to paraffins by nonselective hydrogenation so that it is easily separated through fractionation. The acetylene hydrogenation reactor is placed either within the cracked-gas compression train (front-end hydrogenation) or downstream between the backend deethanizer and ethylene fractionator (backend hydrogenation). Fig. 5 illustrates an ethylene plant with a back-end acetylene converter. In the back-end converter, less hydrogen is present, and this promotes forming an undesirable byproduct—green oil. More green oil is also formed as the catalyst ages.

Green-oil polymer is generated by side reactions of hydrogenating acetylene to ethylene and ethane over the Pd catalyst. It occurs due to the dimerization of acetylene to butadiene followed by oligomerization with successive addition of acetylene to a chain of molecules adsorbed on the Pd surface. Green oil is a mixture, mainly C₄–C₂₀ reactive oligomers of varying composition, with boiling point range of 120–400°C. The heavier fraction remains adsorbed on the catalyst pores; thus, lowering catalyst activity. Steam generation is required to strip away the deposited green oil. The light-end components of the green oil remain in the gas phase; a portion condenses into fine droplets in the gas stream as it cools while leaving the reactor.

The green-oil droplets, carried out with the hydrogenated gas from the reactor, deposit and cause fouling of the downstream heat exchangers, dehydrator beds and ethylene fractionator internals. Eventually, expensive unplanned shutdowns are required to remove the deposited green oil. Recently, high-efficiency L/G coalescers have been applied in this process application. A comparison of different separation technologies, including a liquid ethylene wash, packed-bed separator and de-mister pad separator, found that high-efficiency L/G coalescers provided the best solution in terms of performance balanced by installation cost.⁷

Caustic treatment—red oil. Steam cracking of hydrocarbons for ethylene produces a number of byproducts including the acid gasses, hydrogen sulfide (H₂S) and carbon dioxide (CO₂). An effi-

cient way to remove these gases is with a caustic wash. In this process, an undesirable polymeric contaminant known as red oil. Two mechanisms have been identified in the formation of red oil.⁸

Aldol condensation. Carbonyl compounds formed in the cracking process undergo a condensation reaction in which water and an aldol polymer are generated. Depending on the chain length of the aldol polymer, a viscous liquid to a gummy solid is formed. The red color is caused by the number of double bonds in the reaction product.

Free radical polymerization. In some cases, oxygen and transition metals in the cracked gas can create a different type of polymer formation mechanism known as free radical polymerization. Free radicals are generated from heat, oxygen or transition metal reactions. The free radicals cause chain initiation, followed by chain propagation and finally chain termination.

Caustic towers are often treated with aldol condensation or free radical inhibitors to minimize red oil formation and conversion to larger molecular weight compounds. Despite chemical treatment, red oil can be problematic. Natural and added chemicals can form very stable emulsions. High-efficiency L/L coalescers have recently been applied to commercial systems and were effective in separating red oil from spent caustic. It was important to make this separation directly downstream of the caustic tower to prevent the red oil from polymerizing, as was the case when the coalescer was located downstream of a collection tank. L/L coalescers were effective in removing caustic from the red oil.

Fuel gas—burner protection. Federal and state mandated environmental regulations have been driving the refining and petrochemical industries to reduce nitrous oxide (NO_x) emissions drastically. Advances in pre-combustion burners have allowed significant reduction in NO_x emissions by lowering the temperature in the burner by modifying the oxygen content and/or recycling gases at the furnace inlet. The new burner designs use smaller orifices to achieve the higher pollution reduction. The smaller orifice makes them more prone to fouling.

For ethylene production, a significant contaminant source for fuel gas is the molecular sieve dryers used after the back-end acetylene converters. Fuel gas is used to regenerate the dryers. It strips out the deposited green oil on the molecular sieves, contaminating the fuel gas with the green oil. The contaminated gas causes fouling of the furnace's low NO_x burner nozzles that leads to lower furnace efficiency and more frequent and costly burner tip cleaning.

Burner designs have been developing over the last 20 years and can be categorized for NO_x emissions as follows:

- Conventional burners: 100 ppmv (50 ppm with staged combustion)
- Low NO_x burners: <25 ppmv
- Ultra-low NO_x burners: <10 ppmv

Contamination in the fuel gas can lead to processing problems with the furnace operation. The nozzles can plug, leading to poor furnace performance and, in extreme cases, damage the convective sections of the furnace. At some plants, furnace maintenance has become a costly task requiring burner tip replacement or cleaning every few days.

High-efficiency L/G coalescers have been applied to protect low- and ultra-low NO_x burners.⁹ While many commercial installations exist for refineries, only a few high-efficiency L/G coalescers have been in operation to remove green oil in ethylene plants.

These plants have experienced dramatic improvements in burner service life and reductions in maintenance.

Compressor protection. Compressor lube oil can be contaminated with dissolved and free water as well as gases including H₂S, CO₂ and air; they can reduce the viscosity and lubricity of the oil. These contaminants can also lead to corrosion of metal parts forming solid corrosion products. When unchecked, contaminants in the lube oil will affect compressor reliability. In severe situations, compressors can experience catastrophic failures leading to unplanned outages. Using an oil purifier is an effective way to reduce compressor incidents and ensure reliable service.

Cooling water is injected in some compressors to reduce the formation of organic polymers on the compressor blades by reducing their temperature. Condensate is also formed in the outlet of the compressor and will typically contain water and hydrocarbons. To re-use the condensed water and avoid using more expensive boiler water, the condensate stream can be treated by particulate filters and high-efficiency L/L coalescers. **HP**

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