

PERP Program - Ethylene

New Report Alert

October 2005

Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, **Ethylene (04/05-7)**. To view the table of contents or order this report, please click on the link below:

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Technology Overview

Introduction

Although various alternative routes exist, steam cracking of saturated hydrocarbons (thermal pyrolysis in the presence of steam) is the primary source of olefins. A free radical and chain reaction mechanism generates olefins, with temperatures above 750-800°C required for ethylene formation. The overall reaction is highly endothermic.

Design of commercial olefins plants must deal with a number of constraining conditions:

- Need to supply substantial heat at very high temperature.
- Need to operate at low hydrocarbon partial pressure.
- Need for short residence times to limit consecutive reactions.
- Need to quickly quench the furnace effluent to freeze product compositions.
- Need to provide a high level of energy integration to minimize net energy consumption.
- Need to efficiently make difficult separations between close-boiling components.

Within the pyrolysis section (hot-end) of an olefins plant, once the feed composition (ethane, propane, natural gas liquids, naphtha, gas oils) is set the main design variables are the coil temperature profile, the residence time, and the partial pressure of the hydrocarbons.

The furnace temperature profile is determined by the coil configuration, coil outlet temperature, and burner location within the firebox. Coil outlet temperatures range from 750 to 950°C, with the higher intrinsic reactivity of heavier feedstocks permitting lower temperatures.

Residence time in the cracking coil typically ranges from 0.1 to 0.6 seconds, with longer residence times for heavy than for light feedstocks. Short residence times increase the yield of olefins and correspondingly reduce the yields of aromatics and heavy products. The need for higher heat fluxes and more exotic and costly coil metallurgy place limits on lowering of residence time. The greatest benefits of low residence time are found with heavier feedstocks, while only minor advantages are found with lighter feedstocks.

Low hydrocarbon partial pressures are preferred due to thermodynamics (increase of number of moles as reactions proceed) and the need to avoid condensation reactions which would give heavy products. Furnace exit pressures are generally near atmospheric, with further lowering of hydrocarbon partial pressures by the use of dilution steam. The presence of steam aids in supplying reaction heat and reduces coke deposition on tube surfaces.

Severity of cracking is reflected in single-pass conversion of feedstock. Liquid feeds require higher severity operation to convert heavier, less-valuable intermediate materials to the desired light olefins.

Cracked gas after quenching is treated in the recovery section (cold-end) of the plant to recover and separate the olefin products produced, recycling saturated hydrocarbons to cracking. The recovery section typically includes compression, caustic-washing to remove acid gases, and drying prior to low temperature operations. Hydrogenation removes acetylenic impurities such as acetylene, methyl acetylene, and propadiene. Separation of specification products is conducted using demethanizer, deethanizer, and depropanizer columns in a variety of possible sequences which are tailored to the type of feedstock being cracked and, hence, the range and quantities of products produced. Many-trayed splitter columns make the difficult ethylene/ethane and propylene/propane separations of products from recycle streams. With liquid feedstocks, significant quantities of pyrolysis gasoline are produced, which may require hydrotreating before passing to downstream operations.

Feedstock Selection

As feedstocks become heavier (measured by gravity, boiling range, carbon number, molecular weight, carbon to hydrogen ratio, etc.), the following effects are observed in olefin plant operations:

- Decrease in ethylene yield
- Increase in fuel oil yield
- Decrease in conversion of feed to C₃ and lighter products
- Increase in conversion of feed to C₄ and heavier products

Within the same feedstock type (i.e. naphtha or gas oils), selectivity to ethylene improves as paraffin content increases and declines as naphthene content increases. An increase in naphthenes leads to a higher aromatics yield and, therefore, a higher gasoline yield.

Feedstock selection for ethylene production will also depend on the downstream derivative business. As noted before, the lighter the feedstock (e.g. ethane) the fewer the by-products produced in a steam cracker. Thus, a producer concerned only about feeding his downstream polyethylene business might typically employ an ethane feedstock. The heavy liquid feedstocks (e.g. naphtha and gas oil), in contrast produce a variety of by-products (e.g. propylene, butadiene, butylenes, and aromatics). Larger integrated chemical companies associated with refineries are less constrained and can employ heavier feedstocks since their by-products can be utilized for their derivative business.

In terms of feedstock selection, the following facts need to be taken into account for all olefins producers:

- An ethane plant is an order of magnitude simpler than any other type of cracker (i.e. one feedstock, one product). It would be the choice of a company with limited resources since it has the lowest capital investment.
- A naphtha cracker is more complex with three times the products to sell and involves much more working capital.
- On average, the net ethylene cost of ethane crackers and flexible crackers running on naphtha will be close, but over the years the flexible naphtha cracker will have a lower cost since it can be changed over to the optimum feedstock.

The economics of feedstock flexibility need to be approached from two aspects: (1) the actual investment decision in terms of the total capital cost arising from the basic feedstock choice plus the degree of flexibility that is provided to allow operating changes in the use of different cracker feedstocks, and (2) how that flexibility is utilized once the cracker is in operation.

The dynamics of feedstock price and availability changes and products demand and pricing are the motivating forces for the type of cracker and the degree of flexibility chosen. In practice there are four options:

- Ethane only
- Ethane/propane
- Liquids: naphtha or gas oil or a combination of both
- Flexible cracking with any combination of the foregoing modes

Given a basic cracker feedstock configuration, (i.e. the degree to which alternative feedstocks can be utilized) the issue is one of operating the cracker to produce the lowest cost ethylene at maximum value. Although the details can be complex, the basic relationship is straight forward. The marginal cost of ethylene is the feedstock cost minus co-product and by-product credits plus other variable costs (e.g. utilities.). Extensive data and models are available to address this question.

The key driving forces for feedstock price are natural gas and crude oil, which themselves are interrelated. Co-product values (in the short term) fluctuate with market forces and over longer periods with economic cycles.

Shift in Producing Regions

Little in the way of new ethylene capacity is expected in the Americas or Europe through 2010, with only about 15 percent of new global capacity added in those regions. Over 50 percent of the anticipated new ethylene capacity will be added in the Middle East, especially Iran and Saudi Arabia

(Qatar and UAE to a lesser extent), to take advantage of cheap ethane feedstock. Most of the remaining new capacity will be added in the Asia Pacific region, including India and China.

New mega-scale plants in the Middle East will enjoy low feedstock cost of about \$0.75 per million Btu, equivalent to \$37 per metric ton, for ethane, and long-term feedstock availability. Large plant scale will add the benefit of low specific investment costs (investment per unit of ethylene produced). These factors will combine to give the lowest ethylene production costs worldwide. An additional favorable factor is the proximity to markets in Europe and China.

Alternative Routes/Feeds

Alternative routes to ethylene and feedstocks for conventional steam cracking that are covered in the report include:

- Catalytic ethane dehydrogenation
- Catalytic ethane partial oxidation
- Fischer-Tropsch liquids as steam-cracker feed
- Deep catalytic cracking/catalytic pyrolysis process
- Refinery off-gas recovery
- Methanol to olefins

Technology Details

Detailed process descriptions are provided in the report for natural gas liquids (ethane, propane and butanes), naphtha, and gas oil as feedstocks.

A number of flow schemes are presented and discussed which vary primarily in complexity and flow order through the equipment as a function of the feedstock cracked and the resulting composition of the cracked gas. These schemes are characterized by the relative order of the fractionation towers (demethanizer first, deethanizer first, depropanizer first) and the process location and regime in which hydrogenation of acetylenic compounds takes place.

Highlights of the major ethylene process licensors are provided, along with detailed lists of their project experience in both grassroots and revamp projects.

Future Design Considerations

The consensus among licensors responding (Stone & Webster, Kellogg Brown & Root, Linde, and ABB Lummus Global) is that the technology for ethylene production will continue to be dominated by steam cracking, with the over-riding consideration being design of still larger plants to take advantage of economies of scale in capital costs.

Single train plant capacities of 1 to 2 million metric tons per annum (MMTA) are envisioned, with individual furnace capacities of up to 300 thousand metric tons per annum (KTA) for gas feedstocks and 230 KTA for liquid feedstocks.

In order to optimize the design of mega-capacity ethylene plants, certain adjustments in process temperature, pressure, and concentration profiles may be desirable.

Technology Developments

This section of the report includes the following topics:

- Discussion of selected recent patents
- Improvements in pyrolysis furnaces (furnace materials; anti-coking technologies such as coatings, additives, and inhibitors)
- Integration of gas turbines with cracking heaters
- Advanced system for product recovery from cracked gas
- Methanol to olefins process details

Economics

A comparison of the cases studied is provided, including the following feeds: ethane, ethane/propane mix, ethane/propane with naphtha flexibility, naphtha, gas oil, methanol (for MTO process). Basis is 1.5 billion pounds per year, U.S. Gulf Coast, first quarter 2005.

Atmospheric gas oil feed shows the lowest cash cost and cost of production. However, ethane feed and E/P with butanes feed show somewhat lower cost plus ROCE values. Ethylene from methanol via MTO suffers uniformly higher costs compared to steam cracking. Technology improvements and greater plant scale will likely close this gap somewhat in the future.

Commercial Analysis

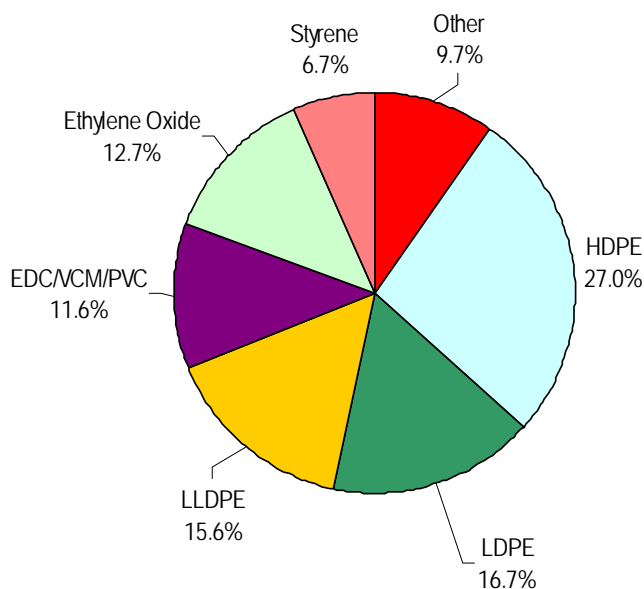
The major chemicals and polymers that are produced from ethylene include:

- Low density polyethylene (LDPE)
- High density polyethylene (HDPE)
- Linear low density polyethylene (LLDPE)
- Ethylene dichloride (EDC), vinyl chloride monomer (VCM), polyvinyl chloride (PVC) and its copolymers
- Polystyrene (PS) and its copolymers
- *alpha*-Olefins
- Fatty alcohols
- Ethylene oxide (EO) and ethylene glycol (EG)

- Vinyl acetate monomer (VAM)
- Ethyl alcohol
- Ethylbenzene (EB) and styrene monomer (SM)

Polyethylene, EDC/VCM/PVC, and ethylene oxide together account for 84 percent of the global demand. This is summarized in Figure 1.

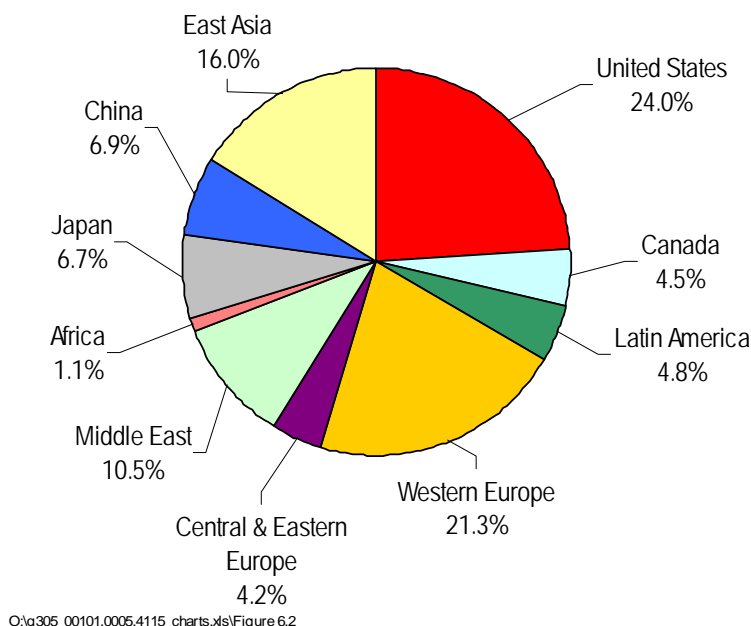
Figure 1
Global Ethylene Demand by Derivative, 2005



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Ethylene end use markets are diverse, owing to the wide spectrum of derivatives. These end use markets include: wire and cable insulation; consumer, industrial and agricultural packaging; woven fabrics and assorted coverings; pipes, conduits, and assorted construction materials; drums, jars, containers, bottles and racks to hold them; antifreeze; and solvents and coatings. Demand growth is therefore dependent on numerous final end markets. The United States, Western Europe, and Japan account for 58 percent of the global demand for ethylene, as shown in Figure 2.

Figure 2
Global Ethylene Demand by Region/Country, 2005



Global data for supply/demand trade, as well as for the following regions, are detailed in the report:

- United States
- Western Europe
- Asia Pacific

Detailed lists of producers and capacities are also provided for each region.

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