ETHYLENE FROM NAPHTHA BY MILLISECOND SM CRACKING WITH FRONT-END DEMETHANIZATION

Aspen Model Documentation

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Process Summary

This Aspen model simulates the production of Ethylene from naphtha by millisecond cracking with front-end demethanization using the M.W. Kellogg process. A plant of capacity equals (500,000 T/yr) Ethylene at 0.93 stream factor is modeled.
About This Process

Millisecond SM cracking (a service mark of M. W. Kellogg) technology differs from a conventional steam cracking process in that a Millisecond cracking system employs straight tubes and bottom-fired furnaces that operate at higher temperatures and shorter residence times than those that are customarily used in steam cracking furnaces for ethylene production.

In comparison with a conventional steam-cracking furnace, a Millisecond furnace produces higher ethylene and butadiene yields and lower fuel oil yield, which is especially important for liquid feedstock. Propylene yields are about the same or even slightly less than those from conventional cracking.

The plant design is based on yield data published by M. W. Kellogg and on SRI’s interpretation of the process information.
Process Definition

In the 1960s, M. W. Kellogg’s R & D Center conducted a series of hydrocarbon steam cracking experiments to determine the effects of temperature, residence time (contact time), and hydrocarbon partial pressure on the olefin yields of various ethylene feedstocks. These experiments, which led to the commercial development of the Millisecond process, showed conclusively that the olefin yields from liquid feedstocks could be increased by 10-20% by high severity, very short contact time cracking. These yield improvements were later confirmed in a 661 million lb/yr (300,000 t/yr) ethylene plant of Idemitsu Petrochemical and several furnace modules of Shell Chemical and Arco Chemical in the United States. Many new ethylene plants based on the Millisecond technology (e.g., furnace revamp for China Petrochemical and new plants for Finaneste, West Lake Polymer, Nigerian National Petrochemical, and others) are now either in operation or at the design and construction stage. At a given cracking temperature and hydrocarbon partial pressure, the optimum range of contact time is between 0.05 and 0.1 sec. This is the contact time range in which the commercial Millisecond process operates. Outside this range, a feedstock is either under- or over-cracked. Over-cracking reverses the upward trends of olefin yields and at the same time causes a rapid increase in acetylene production, which is undesirable. The corresponding operating temperature range for the optimum contact time zone is 871-954°C (1600-1750°F).

To accommodate the high temperature and short contact time operating requirements, the design of a Millisecond cracking furnace differs from that of a conventional steam cracking furnace in the following ways:

• Millisecond cracking coils are made of a large number of small diameter, single-pass tubes, about 1 in. I.D. and 30-40 ft long, in contrast to conventional cracking coils, which are 2.5 to 5 in. I.D., about 90-240 ft long, and composed of straight runs and return bends.
• Burners are fired upward from the furnace floor, parallel to the vertical cracking tubes. In conventional cracking furnaces, the major portion of the heat input is from side-wall burners firing perpendicularly to the cracking tubes.
• The cracked gas from a Millisecond furnace is quenched in two steps: a primary quench in parallel, double-jacketed pipes, each directly coupled to a cracking tube, and a secondary quench in conventional shell-and-tube transferline exchangers. A one-step quench is usually employed in the conventional design. These small diameter tubes in a Millisecond furnace are subgrouped and steam decoked on-line on a rotating basis every few days. After about 30-45 days of on-line operation, an off-line decoking with steam and air is still necessary. A spare furnace is normally provided for off-line decoking.
The plant is subdivided into the following five sections:

- Cracking and quenching
- Compression and demethanization
- Product separation
- Refrigeration
- Gasoline hydrogenation.

We describe the plant operations sequentially below.

**Cracking and Quenching (Section 100)**

The naphtha feedstock is steam cracked in six parallel Millisecond furnaces plus one common spare. The dilution steam-to-feedstock ratio is 0.5 by weight. The furnace outlet conditions are 899°C (1650°F), 25 psia, and 0.08 sec residence time. The parallel furnaces are fired from the floor with recycled CH₄-rich fuel gas. Each furnace is composed of two zones, a radiant zone at the bottom and a convection zone at the top. The radiant zone furnishes the endothermic heat of cracking to the feedstock. The heat absorbed in this zone is equivalent to 40% of the heat input from the floor burners. The remainder of the heat content is absorbed in the convection zone by coils for steam superheating, steam generation, feed-steam preheating, and boiler feedwater preheating. The overall thermal efficiency of the furnaces is 91%. The cross-over temperature from the convection zone to the radiant zone for the feed mix is 649°C (1200°F). As the cracked gas in each cracking tube leaves the radiant zone, it is immediately cooled to below 760°C (1400°F) with preheated BFW in jacketed-pipe exchangers E-102A-R. Most of the high temperature heat, however, is recovered in conventional shell-and-tube transfer-line exchangers (TLXs) immediately downstream of the double-pipe exchangers. High-pressure (1515 psia) steam generated in both types of exchangers is combined and superheated in the furnace convection zone to 510°C (950°F) and used in driving downstream compressor turbines.

Parallel to the naphtha crackers, recycled ethane and propane are co-cracked in a separate Millisecond furnace operating at a furnace outlet temperature of 854°C (1570°F), 25 psia, and 0.3 sec residence time. The cracked gas from the furnace is immediately quenched with BFW to 360°C (680°F) in two parallel TLXs, which generate 615 psia steam. After the TLXs, the two cracked gas streams merge into one, flowing forward toward a primary fractionator (C-101). Before reaching C-101, the temperature of the combined stream is reduced further by a direct quench with a hot oil stream recirculated from the bottom portion of the primary fractionator.

The oil itself is cooled by BFW to generate saturated dilution steam at 165 psia. In the primary fractionator, the fuel oil fraction in the cracked gas is condensed and purged from the system via an adjacent fuel oil steam stripper (C-102). The fuel oil fraction leaves the system via the bottom of C-102. The primary fractionator is refluxed with a gasoline stream recirculated from a downstream water quench tower (C-103), in which steam and a heavy gasoline fraction in the cracked gas are condensed and removed from the system by direct quench with recirculating water streams. The water condensate and gasoline purged from the quench tower are indirectly steam boiled to strip off dissolved gases. The stripped water condensate is reused for dilution steam generation, while the stripped gasoline passes to a downstream depropanizer (C-304) for further fractionation.
Compression and Demethanization (Section 200)

From the quench tower, the cracked gas, at 38°C (100°F) and 16 psia, enters the first stage of a five-stage compression train to be compressed to a final discharge pressure of 525 psia. To avoid polymer formation resulting from temperature rises during compression, the compression ratio between stages is selected so that the discharge temperature of each stage is below 104°C (220°F). Following each stage of compression, the temperature of the cracked gas is brought back to 38°C (100°F) by indirect water cooling. Condensates from compression and post-cooling are decanted of water, steam stripped, and then forwarded to fractionators. Between the third and fourth stages, the cracked gas is scrubbed first with a 15 wt% aqueous solution of monoethanolamine (MEA) to remove 90% of the acid gases, and then with a 15 wt% aqueous solution of caustic to remove the remainder of the acid gases. For solvent regeneration, the rich-MEA solution is steam-boiled at 124°C (255°F) in C-202. A slipstream from the bottom of the regenerator is boiled at a higher temperature, 177°C (350°F), in a reclaimer (E-208). The regenerated lean-MEA solution is recycled. Spent caustic is continuously purged to waste treatment.

A small amount of C₃s purged from the pasteurization zone of a downstream C₃ splitter is returned to the fourth stage of the cracked gas compressor for recompression. Similarly, a small stream of C₂s purged from a downstream C₂ splitter is recompressed at the fifth stage.

At the end of the fifth stage of compression, the cracked gas stream is cooled with water to 38°C (100°F) and then to 13°C (55°F) with propylene refrigerant. Condensate from compression and cooling is removed in a knockout drum (V-205), indirectly steam stripped, and then forwarded to a downstream debutanizer for further fractionation. The cooled cracked gas is dried with molecular sieves in packed tower C-205A (or B). Spent sieves are regenerated with steam-heated hot off-gases. The dried gas is successively cooled further to lower and lower temperatures in a cryogenic cold box with returned off-gases, supplemented by external propylene refrigerant at three additional temperature levels and by ethylene refrigerant at three temperature levels. The lowest temperature reached in the cold box is -138°C (-217°F). This temperature is achieved by passing the H₂-rich and CH₄-rich off-gases through two separate expanders. The power recovered from the expanders is used to recompress these gas streams to 70 psia. Condensates collected in knockout drums in the intermediate stages are fed directly to a downstream demethanizer (C-206), in which dissolved CH₄ is stripped from the liquid phase. The demethanizer operates at 465 psia top pressure and -97°C (-142°F). Reflux for the column is condensed with -101°C (-150°F) ethylene refrigerant. The bottom of the column is reboiled with a condensing propylene refrigerant stream. The net CH₄-rich overhead stream is expanded, as mentioned before, passed through the cold box to recover refrigeration, and then recompressed before being used in the cracking furnaces as fuel. The C₂+ product stream from the bottom of the demethanizer passes to a deethanizer (C-301) in the product separation section of the plant.

A slip stream of the H₂-rich gas coming off the cold box is upgraded from 92 mol% H₂ to 99.5 mol% H₂ in a Pressure Swing Adsorption (PSA) unit for later use in downstream hydrogenation reactors.

Product Separation (Section 300)

The deethanizer separates the product stream into an overhead C₂-and-lighter stream, containing a small quantity of residual methane, acetylene, ethylene, and ethane, and a C₃s-and-heavier bottom stream, containing C₃s, C₄s, and gasoline. The overhead C₂-and-lighter stream passes to acetylene hydrogenator R-301A (or B) to saturate the acetylene into ethane with a stoichiometric amount of hydrogen at 367 psia, 66°C (150°F) in the presence of a Pd-based catalyst supported on alumina. High purity hydrogen for hydrogenation is supplied from the PSA unit shown in Sheet 3 of Figure 7.2. Spent catalyst is regenerated with hot air (not shown on the flow diagram) about once every 6 months. During hydrogenation, a trace of liquid polymers (green oil) is formed and partly entrained in the gaseous C₂ product stream. This oil is removed in alumina-packed guard dryer C-302A (or B) downstream of the acetylene hydrogenator. The guard dryers are regenerated with hot air as needed.
From either of the two guard dryers, the C₂ stream passes to a C₂ splitter (C-303), in which ethylene product is separated from ethane. The splitter operates at 350 psia top pressure and -23°C (-9°F). Residual CH₄ is purged through a pasteurization zone on top of the column and recycled to the cracked gas compressor. A polymer-grade, liquid ethylene product stream, at 99.95% purity, is withdrawn 10 plates below the top plate. The liquid ethylene is pumped to 1425 psia and then exchanges heat with gaseous propylene refrigerant to recover refrigeration. Ethylene leaves the battery limits as a supercritical fluid for use or for transportation to an ethylene pipeline grid for distribution. Ethane recovered from the bottom of the C₂ splitter passes to refrigeration recovery and then to the ethane/propane cracker, F-102.

The C₃+ bottom stream from the deethanizer is depropanized in C-304 to separate C₃s from C₄- and heavier components. The overhead C₃ stream from the depropanizer, which contains propadiene/methyl acetylene (C₃H₄s), propylene, and propane, passes to C₃H₄ hydrogenator R-302A (or B) to saturate the contained C₃H₄ to propane with a stoichiometric amount of high purity H₂. The hydrogenation is conducted at 269 psia reactor top pressure and 82°C (180°F) in the presence of a Pd-based catalyst supported on alumina. As for the acetylene hydrogenators, two post-converter guard dryers are provided to remove green oils formed during hydrogenation. Afterward, the C₃ stream is split in C-306 to produce an overhead polymer-grade propylene product stream and a recycled propane stream at the splitter bottom. As in the C₂ splitter, a pasteurization section is provided at the top of the column to purge out a small amount of CH₄, which had entered the hydrogenator via the H₂ addition. The purged gas is recycled to the cracked gas compressor. The propylene product stream, at 99.5 mol% purity, is withdrawn as a liquid below the pasteurization zone. It leaves the battery limit at about 270 psia and 43°C (110°F). The C₄+ bottom stream from the depropanizer is debutanized to recover a C₄ overhead stream and a C₅-204°C (400°F) gasoline stream at the debutanizer (C-307) bottom. The debutanizer operates at 65 psia top pressure and 41°C (105°F). The C₅s product stream passes to storage, while the gasoline stream passes to the gasoline hydrotreating section of the plant for stabilization.

Refrigeration (Section 400)
Refrigeration is an essential part of a cryogenic demethanization system. It is provided through a propylene-ethylene cascade refrigeration system. The temperatures of the refrigerants are as follows:

- Propylene refrigerant, °C (°F): 10 (50), -18 (0), -32 (-25), and -46 (50).
- Ethylene refrigerant, °C (°F): -59 (-75), -73 (-100), and -101 (-150).

At the end of the last stage of compression for each refrigerant, propylene is condensed with water and ethylene is condensed with propylene.

Gasoline Hydrotreating (Section 500)
Because raw pyrolysis gasoline contains appreciable quantities of gum-forming diolefins (e.g., cyclcopentadiene and isoprene) and alkylbenzenes (e.g., styrene and indene), stabilization by hydrotreatment is usually required, unless the gasoline pool is so large that the pyrolysis gasoline portion is relatively small, i.e., less than 5 vol% of the pool. If hydrotreating is not required, the equipment in this part of the flow diagram may be omitted. However, if the pyrolysis gasoline were to be used for aromatics extraction, a hydrotreating step would be required. We have selected a two-stage hydrotreating process to stabilize the raw pyrolysis gasoline recovered from naphtha cracking. The object of the first stage is to saturate diolefins and styrenes; the purpose of the second stage is to remove sulfur as H₂S because, if present, it tends to concentrate in the raw pyrolysis gasoline stream. Both stages operate in the liquid phase. The first stage uses a Pd-based catalyst operating at 365 psia, 66°C (150°F); the second stage uses a Co-Mo catalyst operating at 615 psia and 288°C (550°F). The H₂ charge is 1,200 scf/bbl of pyrolysis gasoline feed, consisting of 60% from makeup and 40% from recycle. Actual H₂ consumptions are 300 scf/bbl in the first stage and 100 scf/bbl in the second stage. The makeup H₂ is fed through the first stage. Each reactor contains two catalyst beds; reactor temperature in each bed is controlled by product recirculation to the lower catalyst bed. After hydrotreating, the gasoline stream from separator V-502 is
stabilized in column C-501, operating at 50 psia top pressure and 78°C (172°F). Off-gases (H₂ and H₂S) from the top of the column are vented to the fuel gas system via vent drum V-504. Bottoms from the stabilizing column, containing the bulk of the hydrotreated gasoline, are redistilled in atmospheric rerun column C-502. Net overhead from the column is sent to storage as a hydrotreated gasoline product stream, containing 10 ppm maximum sulfur. Bottom residues are blended into the pyrolysis fuel oil.
Although the fuel oil fraction is normally not hydrotreated, it requires blending with fuel oils from other sources to avoid gumming during storage and use.
Process Conditions

The table below summarizes the design bases and assumptions that we have used in preparing the process flow diagram, mass balance, and energy balance for an ethylene plant that employs naphtha as a feedstock and a front-end demethanization product separation sequence. A naphtha feedstock is used as a design basis because it is used in the United States to a significant extent and is nearly the exclusive feedstock for ethylene plants in Europe, Japan, Taiwan, and Korea. The ethylene capacity of the plant is 1,102.3 million lb/yr (500,000 t/yr), representative of a world-scale plant operating at a 0.93 stream factor (8,147 hr/yr). Coproducts from the plant are an H₂-rich stream; a CH₄-rich fuel gas stream, which is consumed in the cracking furnaces; a polymer-grade propylene stream; a C₄s stream, a hydrotreated pyrolysis gasoline stream; and a fuel oil stream. Ethane and propane are recycled and cocracked together to extinction.

The furnace outlet cracking yields of the design basis plant for the wide-range naphtha feedstock at high severity is shown in the Chemistry/Kinetics section of this report.

ETHYLENE FROM NAPHTHA BY MILLISECOND CRACKING
WITH FRONT-END DEMETHANIZATION
DESIGN BASES AND ASSUMPTIONS
CAPACITY: 1,102.3 MILLION LB/YR (500,000 T/YR) ETHYLENE AT 0.93 STREAM FACTOR

Feedstock (wide-range naphtha) characteristics:
Specific gravity (16°C) 0.72
ASTM boiling range 37.2-196°C
Composition
Paraffins 73.5 wt%
Naphthenes 21.0
Aromatics 5.5
Hydrogen content 14.9 wt%
Carbon/hydrogen ratio 5.7
Sulfur content 0.05 wt%
Molecular weight 96

Cracking conditions
Coil outlet temperature 899°C for naphtha;
855°C for ethane-propane
Residence time 0.08 sec for naphtha; 0.4 sec for E-P
Steam dilution ratios 0.5 lb steam/lb naphtha; 0.3 lb steam/lb of recycled ethane-propane
Recycled streams Ethane and propane cracked to extinction
Cracking yields See Table 4.3
Cracking severity High
Radiant zone thermal efficiency 40%
Overall thermal efficiency 91%
Transfer line exchangers (TLXs)
Outlet temperatures 426.7°C for naphtha;
360°C for recycled ethane-propane
Steam pressures 1515 psia for naphtha cracked gas;
615 psia for ethane and propane cracked gases
**Cracked gas compression:**
No. of stages 5
Maximum discharge temperature 104.4°C
Last stage discharge pressure 525 psia
Acid gas removal system A regenerative monoethanolamine (MEA) solution absorption system followed by a caustic scrubber
Absorber location between the 3rd and 4th stages of compression
MEA concentration 15 wt% in water
MEA absorber top pressure 142 psia
MEA absorber top temperature 37.8°C
Acid gas removal by MEA 90%
MEA regenerator top pressure Atm.
Regenerator top temperature 107°C
Caustic scrubber top pressure 140 psia
Caustic scrubber top temperature 37.8°C
Caustic solution concentration 15 wt% in water
Caustic utilization 85%
Cracked gas drying
Dryer location Following last stage of compression
Type of desiccant Type 3A molecular sieves
Moisture loading 6 wt%
Desiccant regeneration cycle 24 hr
Dew point of dried gas -173°C

**Acetylene hydrogenation:**
Catalyst Pd on alumina
Space velocity for both beds 3,500 vol/vol/hr catalyst, STP
Inlet pressure 367 psia
Inlet temperature 65.6°C
H\textsubscript{2}/C\textsubscript{2}H\textsubscript{2} mol ratio 2
Conversion and selectivity 100% C\textsubscript{2}H\textsubscript{2} to C\textsubscript{2}H\textsubscript{6}
Propadiene/methyl acetylene hydrogenation
Catalyst Pd on alumina
Space velocity
1st bed 7,500 vol/vol/hr, STP
2nd and 3rd beds 2,000 vol/vol/hr, STP
Inlet pressure 269 psia
Inlet temperature 82.2°C
H\textsubscript{2}/C\textsubscript{3}H\textsubscript{4} mol ratio 2
Conversion and selectivity 100% of C\textsubscript{3}H\textsubscript{4} to C\textsubscript{3}H\textsubscript{8}

**Pyrolysis gasoline hydrotreating**
First stage:
Catalyst Pd on alumina
Space velocity 3 LHSV (liquid hourly space velocity)
Inlet pressure 365 psia
Inlet temperature 65.6°C
Hydrogen charge ratio 1,200 scf/bbl of gasoline treated
Hydrogen consumption 300 scf/bbl of gasoline treated
Second stage:
Catalyst Co-Mo on alumina
Space velocity 3 LHSV
Inlet pressure to reactor 615 psia
Inlet temperature to reactor 287.8°C
Hydrogen charge ratio 500 scf/bbl gasoline treated
Hydrogen consumption 100 scf/bbl gasoline treated
Physical Property Models and Data

The NRTL-RK thermodynamic package is used.
Chemistry/Kinetics

The table below shows the furnace yield for different feed stocks.

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References

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15 Feb 2000