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Composition Measurement in Ethylene Plants

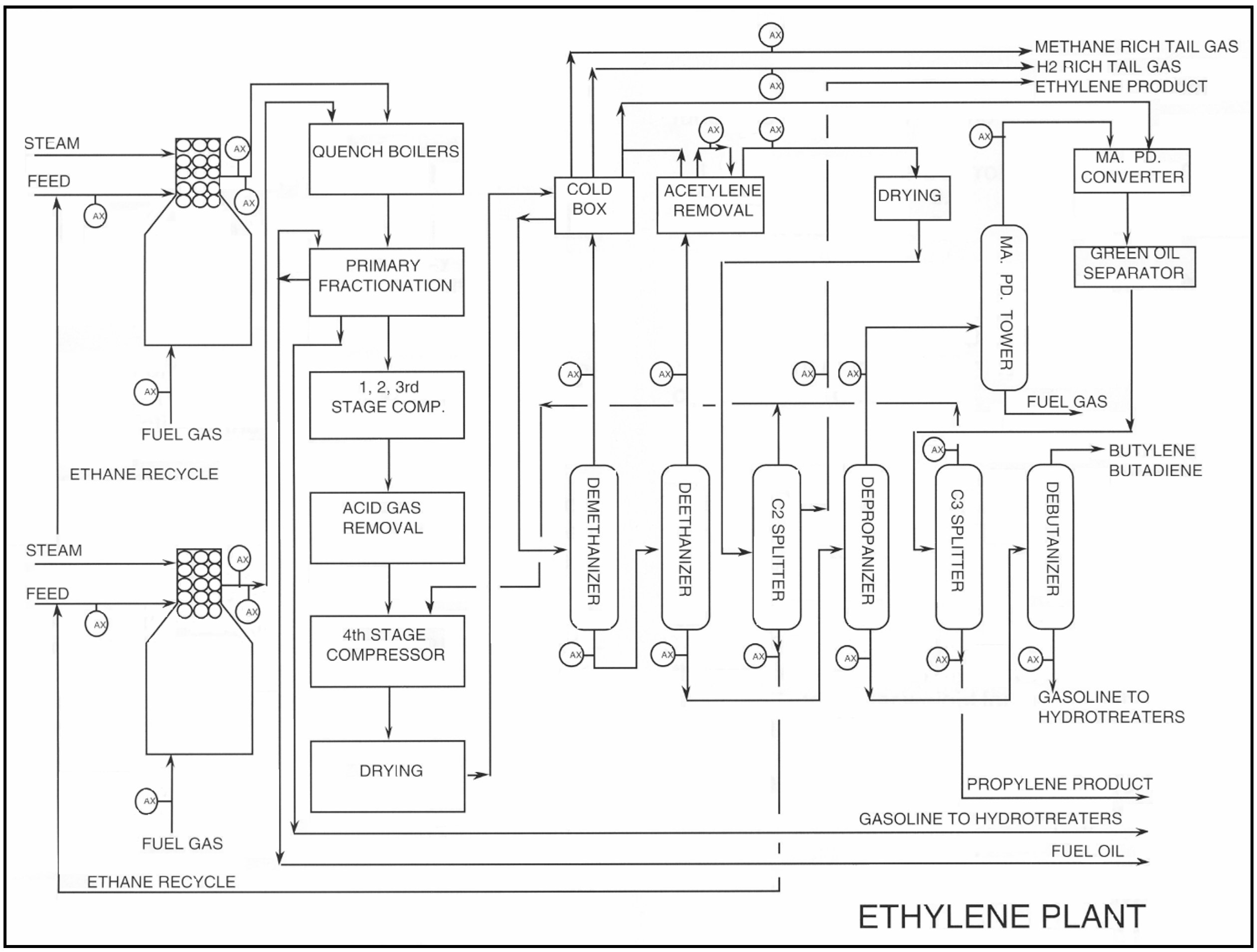
Introduction

An Ethylene Plant is a process for the production of polymer grade ethylene (99.9 vol %). It also produces major byproducts such as propylene (chemical or polymer-grade), a butadiene rich C_4 stream and C_6-C_8 aromatics rich pyrolysis gasoline. The Ethylene Plant is the major supplier of feedstock to the polyethylene plants for the creation of polyethylene plastics.

The first section of the Ethylene Plant is the Pyrolysis Unit (see Fig. 1) that cracks the feedstock into ethylene. The hydrocarbon feedstock is preheated and cracked in the presence of steam in tubular SRT (Short Residence Time) pyrolysis furnaces. The resultant products exit the furnace at 1,400-1,600°F and are rapidly quenched in the transfer line exchangers (TLE) that generate high pressure steam for use in other parts of the plant. The pyrolysis/quench systems are designed to handle the full range of gaseous and liquid feedstocks from the light ethane to heavy naphtha.

The furnace effluent, after quenching, flows to the gasoline fractionator where the heavy oil fraction is removed from the gasoline and lighter fraction (liquids cracking only).

Final cooling of furnace effluents is accompanied by a direct water quench in the quench tower.



The raw gas from the quench tower is compressed in a multistage centrifugal compressor to greater than 500 pounds of pressure. Hydrocarbons condensed in the first charge compression stages are returned to the quench tower while those condensed in the later stages are removed and sent to the depropanizer.

The compressed gas is then dried and sent to the demethanizer. The bottoms go to the Deethanizer.

Acetylene in the Deethanizer Overhead is hydrogenated or, the acetylene can be removed by solvent extraction and recovered. The ethylene/ethane stream is fractionated and ethane leaving the bottom of the Ethylene fractionator is recycled.

The deethanizer bottoms and stripper bottoms from the charge compression system are depropanized. The depropanizer bottoms is separated into mixed C_4 and light gasoline streams. Polymer-grade propylene can be produced by further purification of the depropranizer overhead. Yield data for various feedstocks including ethane (fresh feedstock or recycle) are shown below:

Feedstock	Ethane	Propane	Butane	Naphtha
Ethylene, Wt%	84.0	45.0	44.4	34.4
Propylene, Wt%	1.4	14.0	17.3	14.4
Butadiene, Wt%	1.4	2.0	3.0	4.9
Aromatics, Wt%	0.4	3.5	3.4	14.0

The above yield data present typical high-severity operation to maximize ethylene production. If desired, byproducts may be increased or decreased by altering cracking conditions.

To summarize, an Ethylene Plant consists of several parallel pyrolysis furnaces followed by a cracked gas compressor, an acetylene converter, a Demethanizer, a Deethanizer, a C_2 Splitter, a Depropranizer, a C_3 Splitter and a Debutanizer.

The analyses to be made in an Ethylene Plant will vary slightly from one plant to another; however, the analyses can be divided into three basic groups depending upon their intended use. The three groups are:

1. Analyses that are used in closed-loop control and optimization
2. Analyses that are required for monitoring and alarms
3. Analyses that are required for accounting purposes and data logging

Analysis Used for Computer Control

For the purposes of control, the analyses are divided into two groups as follows:

1. Analyses that are required for closed-loop control of product specifications.
2. Analyses that are required for closed-loop control and optimization of criteria other than product specifications.

The above two groups are divided according to relative importance. Certainly, continuous production of product according to specification is an extremely important function.

Analysis of Product Purity

The principle product of an Ethylene Plant demanding continual monitoring for product impurities are ethylene and sometimes propylene product streams. Product specification analyses are among the more important of the analyses since off-specification product normally cannot be sent to the product pipeline and must be disposed of otherwise - usually to a flare system. Therefore, reliable analyzers for measuring product specifications must be provided. Although product specifications can vary widely from plant to plant, they are typically:

$CH_4 + C_2H_6$	<	0.15%
C_2H_2	<	5 ppm
CO_2	<	10 ppm

The sample for these analyzers should be taken from the Ethylene Product line. The product specification for propylene (if applicable) is typically:

$C_2H_6(MA) + C_3H_8(PD) < 2.0\%$

<u>Ethylene Product Specification Control</u>

To be able to successfully control product purity, it is necessary to be able to measure both the methane and the ethane concentration in the Ethylene Product. The methane impurity in the Ethylene Product is lighter than the light key compound in the C_2 Splitter Overhead Stream. The control point for the methane impurity in the Ethylene Product is the Demethanizer Bottoms Stream. Specifying the methane-to-ethane ratio (CH_4/C_2H_6) in the Demethanizer Bottoms Stream will specify the concentration of the methane relative to ethylene in the C_2 Splitter Overhead and subsequently in the Ethylene Product. A typical full scale range for this analysis ratio on the Demethanizer Bottoms Stream would be

CH_4/C_2H_6 0.0 -> 0.002

The ethane impurity in the Ethylene Product is the heavy key in the C_2 Splitter Overhead Stream. Once the methane concentration in the C_2 Splitter overhead is determined from the Demethanizer Bottoms Stream, the ethane concentration in the C_2 Splitter Overhead can be adjusted or controlled to meet the CH_4 + C_2H_6 specification in the Ethylene Product. A typical full scale range for the ethane analysis is

C_2H_6 0.0 -> 0.2 Vol. %

The acetylene concentration in the Ethylene Product is determined at the effluent of the last stage of the Acetylene Convertors (hydrogenation reactors). Therefore, the objective of controlling these reactors is to control the acetylene concentration in the effluent of the last stage of these reactors. The recommended analyses of these reactors for control are as follows:

Stream	Component	Range
Reactor Feed	C_2H_2	0.0 -> 5000 ppm
	CO	0.0 -> 5000 ppm
Interstage	C_2H_2	0.0 -> 500 ppm
	CO	0.0 -> 500 ppm
Reactor Effluent	C_2H_2	0.0 -> 10 ppm

Additionally, the above analyses for Acetylene Reactors are used for computer optimization; i.e. minimize the amount of ethylene inadvertently converted to ethane through the hydrogenation process in the reactors.

Also, some Acetylene Reactors are difficult to operate; i.e. it is easy to have a reactor "run-away". The above analysis allows supervisory control of the Acetylene Reactors to prevent this from happening.

The analysis of the CO_2 concentration in the Ethylene Product is not usually tied into a computer control scheme. Violation of the CO_2 specification signifies CO_2 break-through from the caustic wash. This CO_2 analysis is used primarily for monitoring and alarm.

Propylene Product Specification Control

Again, successful control of the sum of the two primary impurities in the Propylene Product requires control of the concentration of each of the two individual impurities. The ethane impurity is the lighter than light key compound in the Propylene Product. Therefore, the control of this impurity is the Deethanizer Bottoms Stream.

Specifying the ethane/propylene ratio in the Deethanizer Bottoms will specify the concentration of ethane relative to propylene in the C_3 Splitter Overhead and eventually the Propylene Product.

The propane impurity is the heavy key in the Propylene Product. The control point for the propane impurity is therefore the C_3 Splitter Overhead. Once the ethane concentration in the C_3 Splitter Overhead is determined, the concentration of the propane in the C_3 Splitter Overhead can be adjusted to give the required C_2 + C_3 product specification. Typical ranges for these analysis are:

C_2H_6/C_3H_6 0.0 -> 0.02
C_3H_8 0.0 -> 2.0 Vol %

In the C_3 Splitter, there is sometimes an imported Propane - Propylene (P-P) stream. This means, it will be necessary to also analyze this stream and the Depropanizer Overhead stream to control the ethane in the Propylene Product.

Analysis Used for Additional Control & Optimization

Additional control and plant optimization functions, requiring reliable on-line composition analysis, exist in the furnace area and in the fractionation area. Before specifying the analysis to be used for the additional control and optimization functions, one must first specify the functions to be implemented.

Furnace Control and Optimization

Normally the Cracking Furnace control and optimization functions that require on-line analysis are:

1. BTU Firing Rate Control
2. Velocity Control
3. Conversion Control

BTU Firing Control: For this control, the Fuel Gas is normally analyzed for the following components N_2, H_2, CH_4, C_2H_4 and CO. From the component analysis, the BTU content of the gas can be calculated and used to control the BTU firing rate.

Velocity Control (or Residence Time): For this control, an analysis is made of the cracked gas for the purpose of determining the molecular weight. The sample point for this analysis is located on the effluent of the Secondary Transfer Line Exchanger (TLE). Since speed of analysis is critical for proper control, each sample point is monitored by two analyzers. The first analyzer measures only a few compounds to provide the control system with the information to calculate and estimate molecular weight for the velocity control. The second analyzer provides a slower but more complete analysis of the cracked gas. The analysis from the second chromatograph is used to trim (or update) the estimated molecular weight obtained from the first analyzer.

It is not always practical to have two analyzers on every furnace. What is frequently done is have a dedicated analyzer for each furnace to perform the short analysis and to have a couple of chromatographs that are configured to provide the complete analysis for a number of furnaces each. Furthermore, since the data form the short analysis is so critical for the proper control of the velocity rates, the short analysis analyzers are typically set up to provide back-up capability between each other in the event of analyzer failure.

Conversion Control: Conversion control requires the analysis of the Hydrocarbon Feed to the furnace and the Furnace Effluent or Cracked Gas Stream. The cracked gas analysis used for velocity control is also used to calculate conversion. Again, the partial analysis is used to estimate conversion, with the more complete analysis being used to trim or update the estimated conversion.

Mixed Feed Stream	Cracked Gas Partial Analysis	Cracked Gas Detailed Analysis
CH_4	C_2H_4	H_2
C_2H_4	C_2H_6	CH_4
C_2H_6	C_3H_6	C_2H_4
C_3H_8	C_3H_8	C_2H_6
C_4+		C_3H_6
		C_3H_8
		C_4's
		C_5+

Fractionator Control and Optimization

In order to control the process to insure that the product streams meet specification as discussed earlier, the analyses of fractionator streams are made of the following:

1. Deethanizer Bottoms
2. Demethanizer Bottoms
3. C_2 Splitter Overhead
4. C_3 Splitter Overhead

Additional process streams for possible control in the fractionation area are:

1. Deethanizer Overhead
2. Demethanizer Overhead
3. C_2 Splitter bottoms
4. C_3 Splitter Bottoms
5. Depropanizer Overhead
6. Depropanizer Bottoms
7. Debutanizer Overhead
8. Debutanizer Bottoms

The control of the additional sample points are meant to optimize the recovery of the ethylene and the recovery of the propylene, the reduction of fractionator utility costs and increased throughput where appropriate.

Control of Ethylene Recovery: Ethylene is lost in the Demethanizer Overhead stream and the C_2 Splitter Bottoms. Optimizing ethylene recovery involves control of these two streams. The chromatographic analyses required are the ethylene concentration in the Demethanizer overhead and the ethylene concentration in the C_2 Splitter Bottoms. Typical ranges for these analysis are:

C_2H_4 (Demethanizer Overhead)	0.0 -> 1.0 Vol. %
C_2H_4 (C_2 Splitter Bottoms)	0.0 -> 2.0 Vol. %

Control of Propylene Recovery: Propylene is lost in the C_2 Splitter Bottoms (Recycle Ethane) and in the C_3 Splitter Bottoms stream. As propylene lost in the C_2 Splitter Bottoms is heavier than the heavy key, the control point for the propylene in the C_2 Splitter Bottoms is the Deethanizer Overhead. Control of propylene recovery, therefore involves control of the Deethanizer Overhead and the C_3 Splitter Bottoms. The analyses required for control of propylene recovery are the propylene to ethane ratio in the Deethanizer Overhead stream and the propylene in the C_3 Splitter Bottoms stream. Typical ranges for these analyses are:

C_3H_6 (C_3 Splitter Bottoms)	0.0 -> 5.0 Vol. %
C_3H_6/C_2H_6 (Deethanizer Overhead)	0.0 -> 0.2
C_3H_6 (C_2 Splitter Bottoms)	0.0 -> 2.0 Vol. %

Additional Control of the C_3 Splitter: Improved control of this column could be obtained by the analysis of the C_3 Splitter Feed Stream. The feeds to this column are the Depropanizer Overhead Stream and Alkyl Import Stream (if applicable). In both streams, the compounds for analysis are propylene and propane.

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Depropanizer Control: Control of the Depropanizer is limited frequently to the control of the total C_4's in the Depropanizer Overhead. The chromatographic analysis required for this is the total C_4's in the Depropanizer Overhead stream.

Debutanizer Control: Control of the Debutanizer tower is to the separation of the C_4's from the C_5's and to keep the C_4's out of the Debutanized Gasoline stream.

All of these chromatographic analyses discussed so far were made for the purpose of executing closed-loop control. Even if closed-loop control is not the objective of the plant, these analyses should be made to provide the plant operators with the information they need for proper operation.

Analyses for Monitoring and Alarm

Some chromatographic analyses are for monitoring and alarm purposes only. These analyses are the acetylene and carbon dioxide in the C_2 Splitter Overhead and the methyl acetylene and propadiene (MA/PD) in the C_3 Splitter Bottoms.

Acetylene and carbon dioxide concentration are included in the ethylene production specification. When either exceeds product specification, the product must be flared or otherwise disposed of. It is necessary to detect off-specification product ahead of the C_2 Splitter Overhead accumulator since this accumulator supplies the ethylene refrigeration system. By detecting the off-specification product ahead of the C_2 Splitter Overhead Accumulator, contamination (requiring additional flaring) of the ethylene refrigeration system can be avoided. Conversely, as soon as on-specification ethylene is produced, the ethylene can be delivered immediately as product minimizing the amount of ethylene flared.

The analysis for methyl acetylene and propadiene in the C_3 Splitter Bottoms is a safety measure. MA/PD tend to accumulate in the C_3 Splitter Bottoms. Furthermore, MA/PD tend to explode if their concentrations reach a certain value. The analysis of MA/PD provides the information for a high limit alarm in the C_3 Splitter Bottoms.

Many of the analyses used for control are also used for alarm purposes. These analyses are (a) high limit on all product specifications and (b) high limit in acetylene concentration in the effluent of the Acetylene Convertor.

Analysis For Accounting Purposes

Chromatographs are also used to provide the compositional information needed for accounting purposes. Typical streams monitored for accounting purposes include:

1. Cracking Furnace Fresh Feed
2. Demethanizer H_2 Rich Tail Gas
3. Demethanizer CH_4 Rich Tail Gas
4. C_4 Content of the Import Alkyl Stream
5. Import Refinery Gas

The ethylene rich Import Refinery Gas is introduced into the Cracked Gas Compressor ahead of the fractionation train.

Overall Benefits of Using Process GC's

In addition to the benefits listed throughout this paper, using process GC's as part of an overall advanced control scheme can lead to very impressive benefits. These additional benefits include:

1. Increase the total pounds of ethylene or olefins produced by 5 percent or more when demand and feed supply are not limited.
2. Increase yield of ethylene or olefins per pound of feed by 2-4 percent when feed supply or product demands are limited.
3. Reduce energy consumption per pound of product regardless of feed supply and market conditions.
4. Achieve smoother operation with continuous and automatic coordination of plant-wide changes.
5. Increase process on-stream time by automatically detecting and correcting conditions that could lead to costly shutdowns.
6. Produce a more consistent quality product that assures customer satisfaction.

Furthermore, if process analyzers are coupled with both advanced control and plant-wide optimization schemes, overall plant profitability can improve an additional 5% above those already given.

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Table I: Chromatographic Analyses For An Ethylene Plant			
Stream	**Components Analyzed**		**Anal./SS Probe**
E/P Mixed Feed	C_1,C_2,C_3,C_4+	(%)	1/1 P1
Mixed Feed to Furnace (included recycle streams)	$C_1,C_2=,C_2,C_3,C_4+$	(%)	1/1 P1
Cracked Gas Effluent of Secondary TLE (one analysis per furnace)	$C_2=,C_2,C_3=,C_3$	(%)	1/1+7 P1
Cracked Gas Effluent of Secondary TLE (one analysis per furnace)	$H_2,C_1,C_2=,C_2,C_3=C_4$'s,C_5+	(%)	9/2+7 P1
Fuel Gas to Furnaces	$N_2,H_2,C_1,C_2=$,CO	(%)	9/1 P1
Acetylene Hydrogenation Reactor Feed	CO, Acetylene	(ppm)	5/1 P1
Acetylene Hydrogenation Reactor Inter-stage or BGD	CO, Acetylene	(ppm)	5/1 P1
Acetylene Hydrogenation Reactor Efflu-ent	Acetylene	(ppm)	4/1 P1
Demethanizer Bottoms	$C_1/C_2=$	(%)	1/1 P1
Demethanizer Overhead	$C_2=$	(%)	1/1 P1
Demethanizer -Hydrogen Rich Tail Gas	$H_2,N_2,C_1,C_2=,C_2$,CO	(%)	9/1 P1
Demethanizer -Methane Rich Tail Gas	$H_2,N_2,C_1,C_2=,C_2$CO	(%)	9/1 P1
Demethanizer Bottoms	$C_2/C_3=$	(%)	1/1 P1
Deethanizer Overhead	$C_3=/C_2$	(ppm)	4/1 P1
Ethylene Tower Bottoms	$C_2=,C_3=$	(%)	1/1 P1
Ethylene Tower Overhead	C_1,C_2	(ppm)	4/1 P1
Ethylene Tower Overhead	Acetylene, CO_2	(ppm)	5/1 P1
Ethylene Product	C_1,C_2	(ppm)	4/1 P1
Ethylene Product	Acetylene, CO_2	(ppm)	5/1 P1
Depropanizer Overhead	$C_2,C_3=,C_3,C_4+$	(%)	1/1 P1
Propylene Tower Propylene Product (99.5%)	C_2,C_3	(%)	1/1 P1
Propylene Tower Bottoms	$C_3=,C_4+$,MA, PD	(%)	2/1 P1
Import Alkyl	$C_2,C_3=,C_3,C_4+$	(%)	2/1 P1
Import Refinery Gas	$N_2,H_2,C_1,C_2=,C_2,C_3=,C_3,C_4+$	(%)	9/1 P1

Table II: Summary of Analyses Required for Control of Product Specification

Location	Analysis		Used for Control of	Anal./SS Probe
Demethanizer	$C_1/C_2=$	(%)	C_1 Concentration in Ethylene Product	1/1 P1
C_2 Splitter Overhead	C_2	(%)	C_2 Concentration in Ethylene Product	1/1 P1
Acetylene Hydrogenation Reactor Feed, Interstage, and Effluent	Acetylene	(ppm)	Acetylene Concentration in Ethylene Product	4/1 P1
Acetylene Hydrogenation Reactor Feed and Interstage	CO	(ppm)	C_2 Concentration in Ethylene Product	4/1 P1
Deethanizer Bottoms	$C_2/C_3=$	(ppm)	C_2 Concentration in Propylene Product	5/1 P1
Propylene Tower Overhead	C_3	(%)	C_3 Concentration in Propylene Product	1/1 P1

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