Ethylene as a keystone to the petrochemical industries

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Abstract: State of the art technologies used in producing ethylene are briefly presented including an introduction to steam cracking showing the main six parameters affecting the cracking performance. Different approaches of Ethylene recovery units are also illustrated focusing on the disadvantages and advantages of them. Due to the importance of the ethylene industry, the physical and chemical properties of ethylene are presented as well as different feed stocks used for ethylene plants are shown. Gas cracking, cold fractionation and compression and acid removal drying are illustrated. That discovery that olefins could be produced in large yields from hydrocarbons contained in natural gas or crude oils at a reasonable cost which mainly represents the ethylene industry, has come to be known as the petrochemicals industry. As far as is known, ethylene is the largest volume organic chemical produced today in the industrial world and the most important building block of the petrochemicals industry or as previously entitled as the keystone to the petrochemicals industry. The reorientation of ethylene industry from coal to that depending on natural gas or oils mainly comes from the revolution of ethylene technologies which changed the production capacity around the world from thousands to millions tons, due to successful introduction of raw materials, products, intermediate products and byproducts with the right industrial systems which can handle all the right industrial systems which can handle all in parallel with accepted feasibility studies which mainly depends on the actual demand taking in consideration the expectation of the human needs, development and culture. The effective development and expansion of the petrochemicals industry took place through the availability and devoted efforts of researches and operating staff in the production companies of engineers and technicians in the construction and engineering industry and their suppliers as well as the skilled field erection personnel. The objective of this paper is to present an over view of ethylene industry through different technologies and to assist on understanding the effect of different aspects on this industry.

[Abbas Anwar Ezzat. **Ethylene as a keystone to the petrochemical industries.** *J Am Sci* 2019;15(1):1-5]. ISSN 1545-1003 (print); ISSN 2375-7264 (online). http://www.jofamericanscience.org. 1. doi:10.7537/marsjas150119.01.

Keywords: Ethylene; keystone; petrochemical industries

Physical and Chemical Properties of Ethylene

A- Physical properties

Ethylene as well known is the lightest olefinic hydrocarbon. Its nomenclature or as originally known is “ethene”. At ambient temperature conditions, it is a colorless and flammable gas, it has the same density as nitrogen but with a slightly sweet odor. It is not free in the nature, but it represents the first monomer of almost all the petrochemicals. The attraction of ethylene in the petrochemicals industry comes from the reactivity f its double bond which explains the reasons behind ethylene reactivity in reactions in comparison with acetylene. Table 1 represents a brief illustration to the physical properties of ethylene.

Table 1: physical properties of ethylene. Molecular weight 28.0536

Triple point:

Temperature	-169.19 C
Pressure	0.11 kPa
Latent Heat of fusion	3350 J/mole

Normal boiling point

Temperature	-103.71 C
Latent Heat of vaporization	13540 J/mole
Density of the liquid	20.27 mole/dm^3
Specific heat of the liquid	67.4 J mol^{-1} K^{-1}
Viscosity of the liquid	1.61 x 10^{-4}Pa.s
Surface tension of liquid	0.0164 N/m
Specific heat of the ideal gas (at 25 C)	42.84 J mol^{-1} K^{-1}

Critical Point:

Temperature	9.2 C
Pressure	5.042 MPa
Density	7.653 C
Compressibility factor	0.2813
Gross heat of combustion of the gas at 25 C	1.41 MJ/mole

Limits of flammability at atmospheric pressure and 25C

Lower limit in air	3.7 mole%
Upper limit in air	36.0 mole%

Auto ignition temperature in air at atmospheric pressure: 490 C.

B- Chemical properties

Main chemical reactions of ethylene

a)$CH_2 = CH_2 \xrightarrow{O2\ or\ peroxide\ initiator} low\ density\ polyethylene$

b)

$$CH_2 = CH_2 \xrightarrow{metal\ complex\ (ziegler)or\ metal\ oxide\ catalyst} high\ density\ polyethylene$$

c)$CH_2 = CH_2 + comonomer = \ (e.g. CH_3CH_2CH = CH_2)$

$$\xrightarrow{Metal\ complex\ (ziegler)or\ metal\ oxide\ catalyst} Liner\ low\ density\ polyethylene$$

d)$CH_2 = CH_2 \rightarrow\ oligomers$

Oxidation reactions

e)$CH_2 = CH_2 + 2HCl + \frac{1}{2}O_2 \xrightarrow{CuCl_2, KCL, AL_2O_3\ or\ SiO_2 (230\ C, 3\ ATM, -H_2O)}$

$$CH_2ClCH_2Cl \xrightarrow{-HCL\ (550C, 30\ ATM)} CH_2 = CHCl\ \rightarrow poly\ (vinyl\ chloride)\ and\ copolymers$$

Classical reactions

i)$CH_2{=}CH_2{+}H_2O \xrightarrow{H_3PO_4, SiO_2\ (300\ C, 7\ 0ATM)} C_2H_5OH$ ethyl alcohol

j)$CH_2 = CH_2 + C_6H_6 \xrightarrow{AlCl_3, 4\ 50C, 20\ ATM\ or\ Zeolite, 4\ 00C, 20\ ATM}$

$$C_6H_5CH_2 - CH_3 \xrightarrow{-H_2\ metal\ catalyst} CH_2CH_2 = C_6H_5CH = CH_2 \rightarrow poly\ styrene\ \&\ copolymers$$

Feedstocks and Byproducts of Ethylene Crackers

A- Feedstocks

Feedstocks used as raw materials for ethylene production varies from gas to liquid feedstocks and mainly as follows:

1- Ethane
2- Ethane/Propane
3- Propane/Butane
4- Refinery gases
5- Liquids (Naphtha +Gas oil)

B-Byproducts

Depending on feedstock used, The byproducts are varies depending on the molecular weight of the feedstock and conversion rate.

The byproducts are:

1-Hydrogen
2-Acetylene
3-Methylacetylene and propadiene
4-Propylene
5-Butadiene and Butene
6-Pyrogasoline
7-Pyrolysis fuel oil

Production Of Olefins

Ethylene industry depends mainly on the steam cracking of feedstock while both products and byproducts are related directly to the flow scheme of the plant designed by the ethylene know how owner which depend mainly on the type of feedstock, site location, possible integration and plant owners need.

Main Aspects Affecting Cracking

The theory of steam cracking depends mainly on six parameters which control the quality of the product.

A- Residence time:

Represents the entire length that the unit of gas spends in the cracking coil and as the time decreases the ethylene yield improves but needs increased furnace firing.

B- Hydrocarbon partial pressure

Represents the gas pressure across the cracking coil while decreasing partial pressure gives rise to cracking with low byproducts. Usually dilution steam with calculated ratio is used to lower the partial pressure.

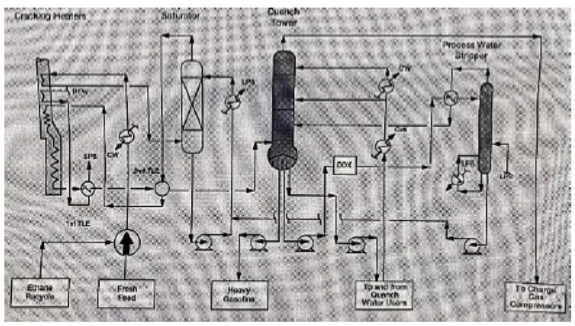

Figure (1) represents general flow scheme of liquid cracking system

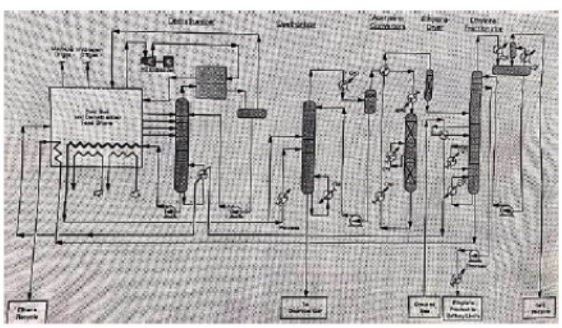

Figure (2) represents general flow scheme of cold fractional system

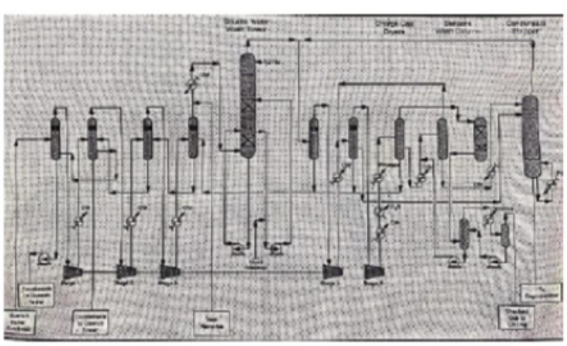

Figure (3) represents compression and acid removal drying

C- Conversion

Is simply defined as the fractional disappearance of the reactant.

D-Severity

Usually takes the adjective mild or medium or high which directly proportional to the temperature of cracking.

E-Selectivity

Selectivity is simply defined as the molal or mass yield of ethylene per mole unit mass of ethane converted.

F- Collesion Factor

An imperical formula defines the relation between the collesion parameter which represents the cracking action with the hydrocarbon partial pressure, cracking temp and residence time.

Molecular collesion parameter =

$$\frac{HC\ Partial\ pressure}{(Cracking\ Temp)^{1.5}}\int_0^{res.time} d\,(res.time)$$

The above formula represents the combination of the above mentioned five parameters and concluding the nature of cracking. Ethylene furnace designers may change one or two parameters but they must keep the overall balance of the formula in order to fulfill the cracking phenomena.

Ethylene Technologies

Ethylene technologies developed by the know how owner in the latest 15 years, all agree on the fact that the successful ethylene producer is that who gains ethylene with minimum cost in and maximum benefits out.

This fact has been considered through the condensed research work together related economical aspects. Ethylene technology in all its ramifications involves the application of scientific principles ant artful elements from several disciplines mainly chemical and mechanical, chemistry and metallurgy.

In spite the fact that ethylene plants contain the same processing steps: cracking heatersection, quench system (cracked gas cooling section), Compression system and fractioning system, all technologies may agree or disagree on the internal sequence of the processing units inside the ethylene plant, but they all meet at one highly pyre ethylene product. The following represents different licensors approach for the sequence of some processing units within the ethylene plant:

A-Demethanizer-First/Deethanizer-First /Depropanizer –First

The final recovery system varies according to the design philosophy of theknow how ownerswith some favoring demethanization as the first step and the others favoring deethanization or depropanization first. Significant amount of the licensors time is spent optimizing the recovery section of ethylene plants. The target is to increase feedstock flexibility and to minimize energy consumption through a number of concepts and are now included in the modern ethylene plant design, mainly high flux exchanger, high efficiency trays, good heat integration system between different equipment in hot and cold sections as well as employing dedicated computerized management control system. Arranging the towers and thus optimizing their operation are another approach taken by the licensors. The different arrangements as mentioned before on the fractionation towers in the recovery scheme are mainly; Demethanizer – First /Deethanizer First /Depropanizer- First. From the chemistry point of view, for the liquid or heavy feed stocks, the removal of heavy portion at first beginning of the plant will lead to a better recovery scheme. In general, the depropanizer - first and deethanizer – first recovery section designs improve system stability and controllability and minimizes potential for exchanger plugging and contaminant freeze out, while demethanizer – first recovery section design shows better energy efficiency, simplifies recovery system, and increases the risk of fouling and plugging. The deethanizer-first design sequence has even better energy efficiency, than the other two configurations. Although all recovery configuration discussed above have their own disadvantages in principle; different licensors made these configurations equally efficient by doing their jobs adequately; that is the saving is not in the choice of configuration but in what to do in the heat integration of the whole plant, Considering the fact that heat integration is dependent on the specific job and site location.

B-Back end /Front end hydrogenation

Important consideration in the recovery section of acetylenic compounds in order to improve the specification of the end product. The front end location for the acetylene converter in the recovery section minimize potential contaminant problems of the hydrogen content of the charge gas and eliminates the need for the addition of reaction moderator since it is already present, but requires larger vessel (conversion reactors) than that of the back end design which only hydrogenate the very low portion of acetylenic compounds existing in the outlet stream of the ethylene fractionator. As the front end design does not need hydrogen production system as it is already present in the cracked gas, the back end design necessitates the existing of not only hydrogen purification unit to produce highly pure hydrogen for the purpose of hydrogenation of the ethylene stream outlet from ethylene fractionator, but also a pasteurization unit at the top of ethylene fractionator to ensure the complete removal of methane from the end product. Both design approaches are considered by different licensors and showed almost equally efficient as they did their jobs adequately by considering the heat integration. Due to the fact that relative cracking economics of each feed stock are directly impacted by the relative pricing of different feed stocks, relative pricing of byproducts and the yield of each feed stock; many improvements within each feed stock processing have been established by licensors in order to minimize the production cost estimate. The following are the brief illustration to some improvements done by ethylene licensors in both hot and cold sections.

Furnace Residence Time

As previously mentioned, short residence time lead to improved olefins selectivity. In general as the residence time decreases the ethylene yield improves and other byproduct yield decreases.

Most licensors prefers the shorter residence time but they offer some variation on the residence time as it has direct impact on the furnace fifing temperature, coil metallurgy, decoking frequency, and severity. They offered millisecond technology which represents the shortest residence time coils, Ultra selective conversion coils (USC), Short Residence Time pyrolysis module (SRT) and High Selectivity Long Run length furnace design (HSLR).

Transfer line exchanger design

The transfer line exchanger (TL#) is typically close coupled to the furnace in order to minimize the residence time in the coil/ TLE transition zone, thus minimizing coking and yield degradation, licensors offered different designs for TLE, mainly depends on double pipe exchanger and shell-tube exchangers. Both design approaches are successfully offered but with different metallurgy and tube in/ out diameter as it represents the main factor affecting coke accumulation.

Dilution Steam/ Saturator

Dilution steam or saturator is used for the purpose of lowering the cracked gas pressure by direct steam injection or by moisturing the inlet gas to the cracker. Both design approaches are successfully offered by licensors with certain design precautions in order to prevent system fouling or any plant trouble shooting.

The Environmental Aspects In The Ethylene Crackers

Ethylene plants which specifically depend on crude or oils as the main feed stock have large number of unit operations of broad spectrum of operating conditions with different chemistry.

For this type of plants, the environmental aspect are mainly concerned with heavy effluents and emissions as well as noise. Both heavy effluent and noise problems are successfully solved by both licensors and equipment suppliers which finally sounds on the price impact of each project and according to each site regulations. On the other hand emission problem in not only ethylene plant but in all other similar industries, still the main problem which forced all designers and operators to find a way to reduce it and to be in accordance with the environmental regulations. Economics are trying to minimize the cost of plants by limiting the plant layout, height of flare, safe area around flaring systems and storage area, etc. While tougher environmental regulations forces the plant owner to do the opposite of what economics need. On the middle, designers are trying to find solution for both targets which should be economically better and environmentally accepted.

On that respect, licensors offered different design for flares, scrapers, incinerators and others which minimize emission problems and they are succeeded on implementing different ways to reduce emissions.

Conclusion

A modern ethylene plant, producing olefins as main product from pyrolysis of hydrocarbon feed stocks involves systems very much akin to both an oil refinery and a cryogenic facility. Environmental aspects have been listed. A comparison between major ethylene technologies has been shown with a brief illustration of main improvements done in both hot and cold sections.

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Biography

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11/28/2018