Lecture 2

Naphtha and Gas Cracking for Production of Olefins

LECTURE 2
NAPHTHA AND GAS CRACKING FOR PRODUCTION OF OLEFINS

Olefins are major building blocks for petrochemicals. Because of their reactivity and versatility, olefins especially the light olefins like ethylene, propylene, butenes, butadiene, etc., there has been tremendous growth in the demand of the olefins. Olefins are finding wide application in the manufacture of polymers, chemical intermediates, and synthetic rubber. Ethylene itself is basic building block for large number of petrochemicals and is quoted as king of chemicals. Some of ethylene manufacturing company and their capacity is given in Table M-VII 2.1. The global ethylene capacity at January 1, 2011, net additions and closings was more than 138 million tones compared with nearly 130 million tones in 2008 [Oil & gas J. Vol 129, 2011]. Global ethylene capacity is given in Table M-VII 2.2.

The steam cracker remains the fundamental unit and is the heart of any petrochemical complex and mother plant and produces large number of products and byproducts such as olefins - ethylene, propylene, butadiene, butane and butenes, isoprene, etc., and pyrolysis gasoline. The choice of the feedstock for olefin production depends on the availability of raw materials and the range of downstream products. Naphtha has made up about 50-55percent of ethylene feedstock sources since 1992. Although basic steam cracking technology remain same for naphtha, gas oil and natural gas, different configuration of steam cracking plant are available from various process licensors [Petrochemical processes, 2003].

Table M-VII 2.1: Top 10 Ethylene Complexes

	Company	Location	Capacity, tpy
1	Formosa Petrochemical Corp.	Mailiao, Taiwan, China	2935000
2	Nova Chemicals Corp.	Joffre, Alta	2811792
3	Arabian Petrochemical Co.	Jubai, Saudi Arabia	2250000
4	Exxon Mobi Chemical Co.	Baytown, Tex.	2197000
5	Chevron Philips Chemical Co.	Sweeny, Tex.	1865000
6	Dow Chemical Co.	Terneuzen, Netherlands	1800000
7	Ineos Olifins& Polymers	Chocolate Bayou, Tex.	1752000
8	Equistar Chemicals LP	Channelview, Tex.	1750000
9	Yanbu Petrochemical Co.	Yanbu, Saudi Arabia	1705000
10	Equate Petrochemical Co.	Shuaiba, Kuwait	1650000

Source: Oil and Gas Journal, 4 Jul 2011

Table M-VII 2.2: Regional Capacity Breakdown

	Ethylene Capacity, tpy
Asia-Pacific	42631000
Eastern Europe	7971000
Middle East, Africa	23357000
North America	34508000
South America	5083500
Western Europe	24904000
Total Capacity	138454500

Source: Oil and Gas Journal, 4 Jul 2011

NAPHTHA /GAS CRACKING

Requirement of steam will depend upon the type of feedstock; the lighter hydrocarbon requires less steam as compared to heavier feedstock. Steam cracking relative cost according to feedstock is given in Table M-VII 2.3. Steam requirement in steam cracker is given in Table M-VII 2.4 [Wiseman, 1986]. Energy requirement pattern for olefin production is given in Table M-VII 2.5 [Gupta, 2000].

Table M-VII 2.3: Steam Cracking Relative Cost according to Feedstock

Feedstock	Relative Investment Cost
Ethane	1.00
Propane	1.15
Butane	1.20
Naphtha	1.45
Atmospheric gas oil	1.65
Vacuum gas oil	1.84

Table M-VII 2.4: Steam Requirement in Steam Cracking

Feed	Kg steam/kg of hydrocarbon
Ethane	0.2 – 0.4
Propane	0.3 – 0.5
Naphtha	0.4 – 0.8
Gas Oil	0.8 – 1.0

Table M-VII 2.5: Energy Requirement for Olefin Production

Feedstock	Specific Energy Consumption	
	Kcal/kg of Ethylene	Kcal/kg of Olefin
Ethane	310	3,050
Propane	4,100	3,050
Ethane/Propane	3,600	3,300
Naphtha	5,000	3,050

Modern ethylene plants incorporate following major process steps : cracking compression and separation of the cracked gas by low temperature fractionation. The nature of the feed stock and the level of pyrolysis severity largely determine the operating conditions in the cracking and quenching section. Various steps involved in the pyrolysis of naphtha and separation of the products are discussed below. In case of gas cracking separation of ethane and propane from natural gas is involved. Flow diagram for pyrolysis of napththa is given in Figure M-VII 2.1.

Hot Section

It consists of convection zone and radiant zone. In the convection zone, hydrocarbon feed stock is preheated and mixed with steam and heated to high temperature. In the convection zone the rapid rise in temperature takes place and pyrolysis reaction takes place. The addition of dilution steam enhances ethylene yield and reduces the coking tendency in the furnace coils. The production of the pyrolysis reaction consists of a wide range of saturated and unsaturated hydrocarbons.

Quench Section

To avoid subsequent reaction the effluent are fixed in their kinetic development by sudden quench first by indirect quench by water to 400 – 450 ^{o}C in transfer line exchanger or quench boiler. This is a large heat exchanger that is a bundle of metal tubes through which the gases pass and around which is circulated water under pressure. The hot water produced is used to generate steam for use in the plant. In the next step the quench is done by heavy product of pyrolysis.

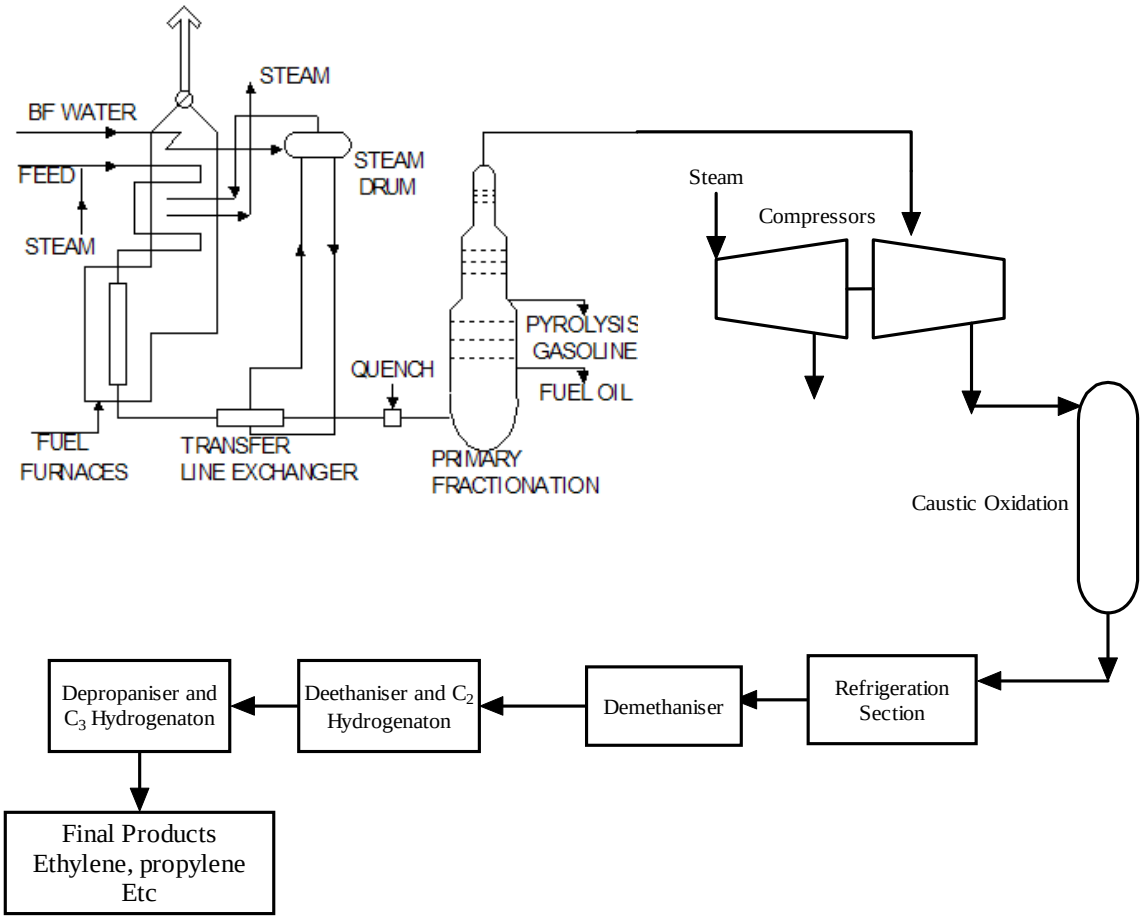


Figure M-VII 2.1: Typical Naphtha Cracker Plant

HOT SECTION

Convection Zone	Feed stock is pyrolised and the effluent conditioned
Radiation Zone	The product formed are separated and purified
Quench	To avoid subsequent reaction the effluents are fixed in their kinetics development by sudden quench.
I Indirect	Indirect quench by water to 400-500^{o}C generation of high pressure steam
II Direct	Direct quench by heavy residue by-product of pyrolysis
Primary Fractionation Column	Separation of light products of pyrolysis as top and bottom as pyrolysis product
Compression	Compression of light products

Caustic Scrubbing and Drying	Scrubbing with caustic followed by molecular sieve adsorption to remove sulphur compounds, mercaptan, etc.

Cold Section

After compression, caustic scrubbing and drying the light effluents enter the cold section of the unit which performs the separation of (I) hydrogen to various concentration (ii) ethyllhene containing 99.4percent (iii) 95percent propylene (iv) A C_4 cut containing 25-50percent butadiene (v) pyrolysis gasoline which is rich in aromatic hydrocarbons.

The complexity of the separation section of a cracker increases markedly as the feed changes from ethane.

COLD SECTION	• Hydrogen separation • Ethylene separation 99.9percent • Propylene separation • A C_4 cut containing 25-50percent butadiene • Complementary fraction of pyrolysis gasoline rich in aromatic hydrocarbons
Demethaniser	Methane condensed at top around – 100^0C pressure 32 Pa
Deethaniser	Separation of C_2 cut;(Ethane and ethylene) Acetylene eliminated by selective hydrog-nation Catalyst : Palladium or Nickel 40-80^{o}C, 3 kPa
Separation of Ethylene	Ethylene is fractionated and unreacted ethane recycled
Depropaniser	C_3^+ cut from bottom of deethaniser is fractionated. C_3 cut from top of depropaniser is selectively hydrogenated to remove methyl acetylene and propadience. Propylene content 95percent. Separation in supplementary column for more pure propylene.
Removal of propane from propylene	Separation in supplementary column for more pure propylene
Debutaniser	Separation of C4 stream from C_5+ stream

REACTIONS IN STEAM CRACKING

The reactions involved in thermal cracking of hydrocarbons are quite complex and involve many radical steps. The thermal cracking reaction proceeds via a free radical mechanism. Two types of reactions are involved in the thermal cracking (i) primary cracking where the initial formation of paraffin and olefin takes place (ii) secondary cracking reaction where light products rich in olefins are formed. The total cracking reactions can be grouped as follows:

- Initiation reaction.
- Propagation reaction.
- Addition reaction.
- Isomerization reaction.
- Termination reaction.
- Molecular cyclization reaction

OPERATING VARIABLES OF STEAM CRACKING

The main operating variables in the pyrolysis of hydrocarbon are composition of feed stock, reaction temperature, residence time, hydrocarbon partial pressure and severity.

Composition of Feed Stock

Naphtha are mixture of alkane, cycloalkanes, and aromatic hydrocarbons depending on the type of oil from which the naphtha was derived. The group properties of these components greatly influence the yield pattern of the pyrolysis products. A full range naphtha boiling range approximately 20 to 200oC would contain compound, with from 4-12 carbon atms. Short naphtha boiling point range from 100-140^{o}C and long chain naphtha boiling point lies around 200-220^{o}C. The steam cracking of the naphtha yields wide variety of products, ranging from hydrogen to highly aromatic heavy liquid fractions. The thermal stability of hydrocarbons increases in the following order: parafins, naphthenes, aromatics. Yield of ethylene as well as that of propylene is higher if the naphtha feed stock is rich in paraffins. Effect of feed stock on the yield of various gases is given in Table-5. It may be seen that relative production of ethylene decreases as the feed stock becomes heavier. The percentage of pyrolysis gasoline C5-200^{o}C cut

increases. Simultaneously butadiene yield varies slight with feed stock in the treatment of liquid petroleum fractions.

Furnace Run Length

Furnace run length can be calculated from the equation [Chamber & Potter, 1974]

$$\text{Run length} = \frac{T_{md} - T_{mc}}{\Delta T_m / day}$$; T_{md} = maximum allowable tube skin temperature

ΔT_m /day= Average rise in tube skin temperature per day

T_{mc} = maximum metal skin temperature in the clean, uncoked condition

For any feedstock the heater section run length depends on the pyrolysis coil selectivity, cracking severity and transfer line exchanger design. Run length varied between 21 - 60 days for gas-based furnaces and 21-40 days for liquid feed based furnace [Wysiekierski & Fisher, 1999].

Pyrolysis temperature and Residence Time

The effluent exit temperature is generally considered a significant indicator of the operation of a furnace. As the furnace exit temperature rises, the yield also rises, while the yields of propylene and pyrolyis gasoline (C_5-200^oC at) decrease. With respect of ethylene yield, each furnace exit temperature, correspond to an optimum. The highest ethylene are achieved by operating at high severely, namely, around 850^oC with residence time ranging from 0.2 to 0.4s However, operating at high temperature results in high coke formation.

Partial Pressure of Hydrocarbon and Steam to Naphtha Ratio

Pyrolysis reaction producing light olefins are more advanced at lower pressure. Decrease into the partial pressure of hydrocarbons by dilution with steam, reduces the overall rate reaction rate, but also help to enhance the selectivity of pyrolysis substantially in favour of the light olefins desired. Other role of steam during pyrolsis is (1) to increase the temperature of feed stock (2) reduction in the quantity of heat to be furnished per linear meter of tube in the reaction section (3) to remove partially coke deposits in furnace tubes.

The ethylene yield decreases as the partial pressure of hydrocarbon increases. The effect of H_2O/naphtha on ethylene yield is given in Fig.4 for economic reason a value of 0.5 to 0.64 of steam per tonne of naphtha is generally adopted as the upper limit.

Severity and Selectivity Concept

Severity is often used to describe the depth of cracking or extent of conversion. The definition of severity varies with the different manufactures and may differ accordingly to the type of hydrocarbon treated. In the case of steam cracking of the ethane and propane, it is convenient to express the severity of the operating conditions in terms of feed conversion. At very high severities, the methane and ethylene yield level off, while those of propylene and C4 cut reach a peak and then decline consequently. The ratio of ethylene and propylene yield increases with severity, which hence favours the formation of ethyelene. The relative production of C^{5+} cut passes through a minimum and at the very high severity tends to increase.

Modern ethylene plants are normally designed for near maximum cracking severity because of economic considerations.

ETHYLENE FURNACE DESIGN

Pyrolysis furnace design during the last three decades made significant development. Prior to 1960, the ethylene pyrolysis furnaces were box type with horizontal radiant tubes. The capacity of these furnaces were small capacity (40 MM lb/y) today standards (250 MM/lb/y). High thermal efficiency furnace design can contribute greatly to minimum overall plant utility costs. Higher efficiency can be achieved by (i) Upgrading of pyrolysis furnace capacity (ii) increasing cracking severity (iii) improving ethylene selectivity (iv) improving thermal efficiency (v) reducing downtime for decoking (vi) reducing maintenance cost. This can be achieved by radiant coil with shorter residence time and lower pressure drop, combustion air preheating and short residence time. Small diameter coils coupled with increased dilution steam, with use of booster compressors to reduce furnace outlet pressure can increase efficiency ethylene selectivity. Radiant coils with a short residence time and low hydrocarbon partial pressure give higher ethylene selectivity.

COKE FORMATION DURING PYROLYSIS AND DECOKING MEASURES

Pyrolysis of any hydrocarbon feedstock is always accompanied by coke formation, which deposits on the walls of the tubular reactor. Under typical operating conditions, the coke

formation in naphtha pyrolysis is about 0.01 wt.% of the feed [Towfighi et al., 2001]. The coke deposits on the walls of reactor reducing the overall heat transfer coefficient and increasing the pressure drop across the reactor. This results in gradual decrease with run time of both the reactor tube metal temperature and the pressure drop across the reactor necessitating periodic shut down. The coke formation inside the tube will depend upon (i) characteristics of feedstock and the coking precursor (ii) hydrocarbon partial pressure (iii) thermal condition of coil (iv) mass velocity which controls the dynamics of gas film close to the wall. Controlling coking rate permits increasing the severity of the furnace to increase conversion rate, reducing the cycle rate and unloading downstream limiting equipment which increases throughput [Burns et al., 1991].

Frequent decoking operating result in loss of production effect the coil life and increase fuel and utility costs. Run length between two successive decoking varies according to the installation and the type of feed stock, but can be estimated at a few weeks on the average. In ideal conditions, a furnace operating on naphtha can run for go days without decoking. However, run length is always shorter due to the inevitable fouling of the quench boiler. In practice run length is as long as 90 days on ethane feed stock, 65 days naphtha and 40 with gas oil [Chauvel, A., Lefebvre, G., "Petrochemical Process" Vol. 1, Institute Francais du Petrole Publications Editions Technip, 27 Rue Ginwux, Paris, 1989].

Various approaches for coke mitigation are based on reduced coke production in the coils and increased rates of coke removal or removal of coke precursors during pyrolysis [Wysiekierski et al. 1999]. By using improved metallurgy and innovative coating systems, ethylene producers seek to improve unit reliability, increase carburization resistance, extend processing run length, reduce downtime and plant shut downs, increase yields and throughput, extend furnace tube life [Wysiekierski & Fisher, 1999].

Mechanical decoking, steam air decoking are the method used for decoking. Mechanical decoking processes takes 4-7 times longer than steam air decoking. The principal method of decoking with steam air are spalling and burning. The coke is burnt in the presence of steam and air at temperature from (600-800^{o}C).

TRENDS IN TECHNOLOGICAL DEVELOPMENTS OF STEAM CRACKERS FOR PRODUCTION OF ETHYLENE

From the late 1960s through the 1970, the petrochemical industry built a generation of new steam crackers with an ethylene capacity of several million tonnes capacity. Older plant consists of typically 10-17 small furnaces with radiant coils having residence time 0.4-0.6 sec, thermal efficiency below 90percent, central waste heat recovery system and nitrogen oxide (NO_X) emissions 75-100 ppm. Present day olefin plants have capacity more than 1,000,000 tonnes per year ethylene produced with 5-7 modern cracking furnaces using twin-cell designs. Short residence time and radiant coil smaller diameters increase yields. The higher selectivity of modern coils reduces specific energy consumption. The modern olefin plants have better ethylene selectivity and improved health, safety and environment standards by incorporating current emission and safety standards [Feigl & Schmidt, 2007].

Major energy improvements by revamp or by replacing the existing furnace sections can be achieved by [Fiegel & Schmidt, 2007]:

- Increased thermal efficiency
- Higher radiant efficiency and less excess air by new burner technology and better instrumentation
- Reduced heat losses due to fewer and bigger furnace units or new refractory
- Higher yields by new radiant coils, reducing specific energy demand
- Higher availability by application of new and highly reliable technology, reducing losses due to unplanned shutdowns.

Performance of the steam cracking furnace can be upgraded by: (i) increasing furnace capacity (ii) increasing cracking severity (iii) improving ethylene selectivity (iv) improving thermal efficiency (v) reducing downtime for decoking and reducing maintenance

REFRENCES

1. Burns, K.G., Ciarella, C.T., Rowe, J.L., Sigmon, “Chemicals increase ethylene plant efficiency”, Hydrocarbon Processing, January 1991, p. 83.
2. Chambers, L.E., Potter W.S., “Design ethylene furnace part I, Maximum ethylene”, Hydrocarbon Processing, January 1974, p. 121.

3. Chauvel, A., Lefebvre G., “Sources of Olefinic and aromatic hydrocarbons’, Petrochemical Processes, 1985, Volume I, edition Technip, p. 129.
4. Desai D.M., “New technologies for Petrochemicals part-1”, Chemical Business, Sep.-Oct. 4, 25 1991.
5. “Energy Conservation Process Industry”, Energy Conservation Department, Engineers India Ltd., New Delhi, 1992.
6. Feigl, J., Schmidt, G. “Consider furnace replacement for existing olefin units”, Hydrocarbon Processing, June 2007, p. 45.
7. Gupta, A.K., Invited lecture, AICTE Staff development programme on Hydrocarbon Engineering, IIT Roorkee, 3-22 January, 2000.
8. Gupta, A.K., Invited lecture, QIP short term course on Advances in Hydrocarbon Engineering, IIT Roorkee, 23 June-4 July, 2003.
9. Mall, I.D. “ Petrochemical process technology”, First edition, New Delhi, Macmillan India 2007
10. Petrochemical processes, 2003. Hydrocarbon Processing March 2003
11. Towfighi, J., M. Sadramdi, A. Niuei, “Simulation of furnace length”, Petrochemical Technology, quarterly Autumn, 2001, p. 137.
12. Wiseman, P., “Petrochemicals”, 1986, Ellis Horwood Ltd, Chichester, p. 33.
13. Wysiekierski, A.G., G. Fisher, C.M. Schillmoller, “Control coking for olefins plant”, Hydrocarbon Processing, January 1999, p. 97.