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<tr><td rowspan="3">KLM Technology Group

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#033, Jalan Bayu 8/1,
Taman Nusa Bayu,
79200 Iskandar Puteri,
Johor, Malaysia.</td><td colspan="2">BEST PRACTICE FOR
ETHYLENE FURNACE DECOKING

(BEST PRACTICES)</td></tr>
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SCOPE

This Best Practice specifies the major requirements of ethylene furnace decoking provides guidelines on some issues.

Ethylene is produced by thermal cracking of hydrocarbons (Ethane/Propane/Butane/Naphtha/Gas Oil etc.) in radiant coils of furnace section. Furnace effluents from radiant coils are immediately quenched in transfer line exchangers (PTLE, STLE, TTLE etc.) to arrest the chain reaction avoiding secondary reaction. Coking is term used to describe laying down coke or carbon on process sides of tubes in cracking heaters coke insulates tubes and causes metal temperatures to rise coke reduces flow coils.

Non-optimal decoking results in lower availability of furnaces. In general, one in three of the ethylene plants are furnace limited, therefore improving the decoking process can increase plant utilization. In some sites, utilization improvements of several percent have been achieved by improving the decoking process.

The focus of this document is decoking methods in ethylene cracker furnaces. For sites that apply steam-air decoking, and existing procedures should be reviewed with this document since it contains guidelines for safe and complete decoking.

INTRODUCTION

Furnace technology is an area of active research. The high-energy consumption, capital and maintenance cost of the current cracking furnace are a driving force to develop improved conversion routes. The pyrolysis of hydrocarbons for the production of petrochemicals is almost exclusively carried out in tubular coils located in fired heaters. Steam is added to the feedstock to reduce the partial pressure of the hydrocarbon in the coil. The reactions that result in the transformation of saturated hydrocarbons to olefins are highly endothermic and require temperatures in the range of 750 to 900 degrees C depending on the feedstock and design of the pyrolysis coil.

Prior to the mid 60’s all furnaces were fired with a very large number of wall burners spaced on about six-foot centers in the horizontal walls and facing the row of radiant tubes. Thereafter most designers working with burner manufacturers developed the capability of firing cracking furnaces mainly or exclusively with a much smaller number of floor burners. Some Technologies still utilize wall burners for a small portion of the heat fired. This change was made possible because of much better control of the excess air within the firebox.

During 1960s the first vertical radiant tube pyrolysis cracking furnace was commissioned at Esso’s plant in Koln, Germany. Shortly thereafter essentially all new cracking furnaces were designed with vertical tubes. The driving force was the much lower investment cost required for vertical tube furnaces. The residence time for these furnaces was about 0.3 seconds. Typical tube ID was about 4 to 5 inches.

By 1965 manufacturers (initially Duraloy in the US) started to produce cast tubes. A number of plants tried them with little success. Finally it was realized that the dross at the tube ID was causing very rapid coking and very poor tube life. Then the manufacturers found a way to machine the tube ID to a smooth, imperfection free, surface and their performance greatly improved.

During the late 70’s and 80’s the radiant tube diameters used in cracking furnaces decreased. The smaller diameter tubes had a higher surface to volume ratio, which allowed the heat necessary for cracking to enter the tubes in a much shorter tube length. This allowed the cracking to take place in a much shorter residence time which gave much better yields of the desired products (mainly ethylene, propylene and butadiene). Ultimately, about 1979 both Kellogg and Esso (Exxon) developed furnaces with multiple parallel radiant tubes each about 40 feet long and 1 to 1.5 inches ID.

Coke is a normal by-product of the steam cracking reaction. A heater is said to be coked up or in need of “De-coking” when tube temperatures attain 1050°C (the radiant tube design limit maximum temperature is 1125°C), increase in TLE outlet temperature, increase in radiant coil/TLE pressure drop.

An accurate simulation of the decoking operation of a steam cracker requires an adequate reactor model and an adequate furnace model. A complete reactor model consists of a set of continuity equations for the process gas components, not only in the process gas bulk flow, but also in the coke layer that is being removed.

The purpose of decoking is to remove coke/carbon from cracking furnace system by controlled burning with steam and/or air, reduce thermal resistance to heat transfer between firebox and process fluid inside radiant tube and reduce process pressure drop.

Decoking Reactions

$C + O_2 = CO_2$ (1)
$C + CO_2 = 2CO$ (2)
$C + 2H_2 = CH_4$ (3)
$C + H_2 = CH_4$ (4)
$C + H_2O = CO + H_2$ (5)
$CO + H_2O = CO_2 + H_2$ (6)
$H_2 + 1/2\ O_2 = H_2O$ (7)

Design Constraints

The typical modern pyrolysis furnaces consist of a rectangular (important) firebox with a single or double row of vertical tubes located in the center plane between two radiating refractory walls. The heat transfer to the tube is affected largely by radiation and only to a small degree by convection. The firebox temperature is typically in the range of 1200 degrees Centigrade.

1. Process Chemistry

To fully understand the furnace design constraints a review of process chemistry is required. When a hydrocarbon feedstock is undergoing pyrolysis a multitude of reactions happen simultaneously, but for practical purposes a simplified outlook will explain many of the end results in which are of primary interest.

Hydrocracking of Ethane

$$C_2H_6 = CH_3^* + CH_3^* \tag{8}$$

$$CH_3^* + C_2H_6 = CH_4 + C_2H_5^* \tag{9}$$

$$C_2H_5^* = C_2H_4 + H^* \tag{10}$$

$$H^* + C_2H_4 = H_2 + C_2H_5^* \tag{11}$$

$$C_2H_6 = C_2H_4 + H_2 \tag{12}$$

The process chemistry review reveals at least three design requirements:

a. Low Pressure

The predominately desired reaction is :

$$C_2H_6 = C_2H_4 + H_2 \tag{13}$$

Any time the moles of products are larger than the moles of reactants the equilibrium favors low pressures.

b. Low Hydrogen Partial Pressures
To reduce the unwanted hydrogenation reaction, lower hydrogen partial pressures would produce more of the desired products.

c. Short Residence Time
To reduce the unwanted condensation reaction, shorter residence times would produce more of the desired products.

2. Heat of Reaction

The reaction is endothermic and requires high temperatures. Couple the heat of reaction with the low pressure requirement - size and length of coils are dictated.

Diameter To Length Ratio :

Q = U A DT **(14)**

1) If the pressure drop is fixed Q is set by the diameter of the coil.
2) U and DT are fixed.
3) A determines the length of the coil.

Diameter To Length Ratio
1) 1 inch diameter is approximately 40 feet.
2) 2 inch diameter is approximately 80 feet.
3) 3 inch diameter is approximately 120 feet.
4) 4 inch diameter is approximately 160 feet.

3. Metallurgy

Table 1. Typical Metallurgy Constraints

Trade Name	Composition	Temperature limits	Developed	Carbon Pick Up
HK 40	**25/20 : Cr/Ni**	**1830 F 1000 C**	**Late 1960's**	**1% at 1055 C**
HP Modified	**25/35 : Cr/Ni**	**2,060 F 1125 C**	**Early 1970's**	**1% at 1125 C**
35/45	**35/45 : Cr/Ni**	**2100 F 1150 C**	**Mid 1980's**	**1% at 1155 C**

4. Flame pattern/Fire Box

The pyrolysis reaction is endothermic and time dependent reactions. The flame pattern and the resulting heat flux can have the net effect of changing the effective length of the coil. If the heat flux is not uniform the coil's effective length can be reduced. If heat flux is not uniform hot areas can cause over-cracking and shortening coil life.

Figure 1. Flame Pattern Constraints

The shape of the flame is determined by burner designers according to heat input requirements by the technology provider. The shape of the fire box will affect the flame pattern and heat flux. Deviation from rectangular has not proved to be successful.

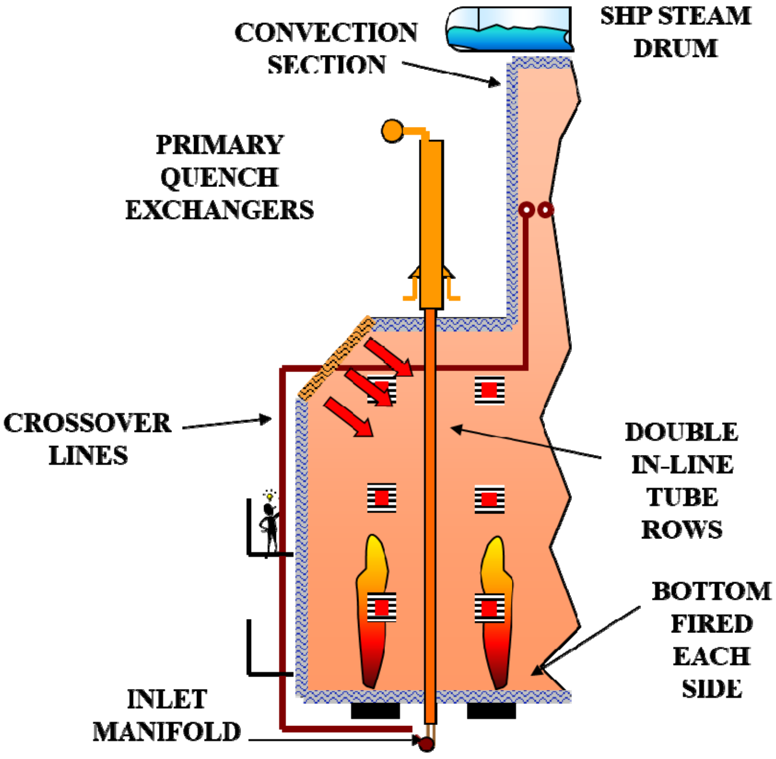

Figure 2. Fire Box Shape

Comparison of current Design

It is the diameter and length of the tubes and the manner in which they are interconnected to and from the pyrolysis coil which determine to what extent a particular design will be characterized by an optimum combination of pyrolysis parameters. The design calculations applied to pyrolysis coils are necessarily complex since heat transfer and chemical reaction are involved. Various options exist for the specific design of a pyrolysis coil, and this accounts for the variety of industrial pyrolysis furnaces presently in operation.

If short residence time is considered the single most important objective, then a short coil with tubes of small diameter will be considered. If a combination of high capacity, medium resident time and low hydrocarbon partial pressure is judged to be most beneficial, then a relatively larger tube will result.

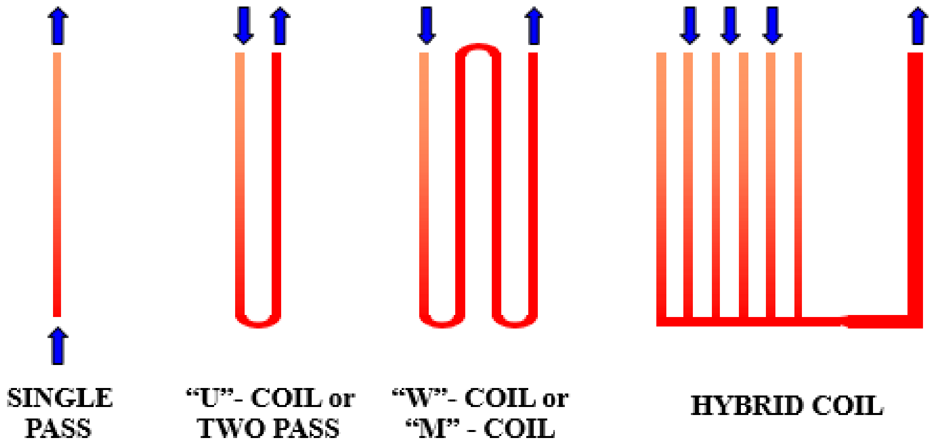

Figure 3. Types of Furnace Coils

Typical of Current design of Furnace

1. Short Residence Time - One pass of uniform size- Fire box floor to roof orientation.

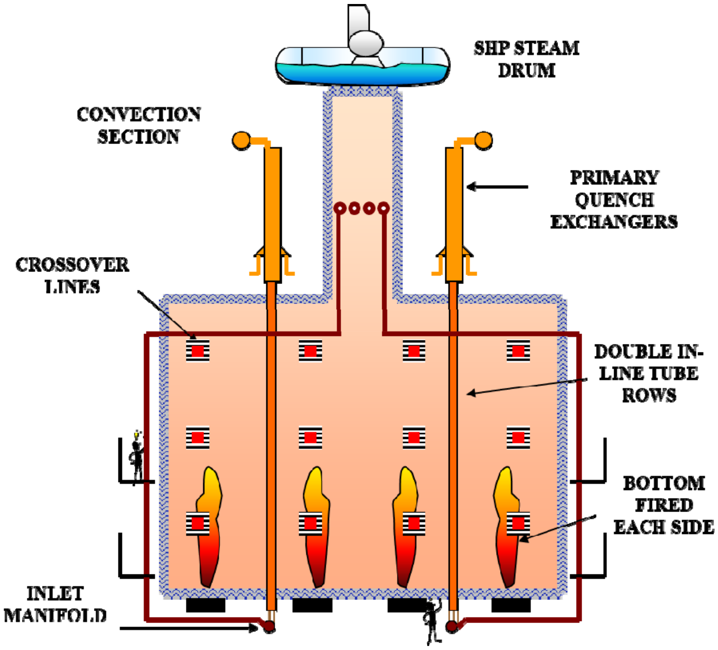

Figure 4. Typical End View Furnace Single Pass

2. U Sweep Bends - one or more passes of uniform size - U configuration - fire box roof to roof orientation.

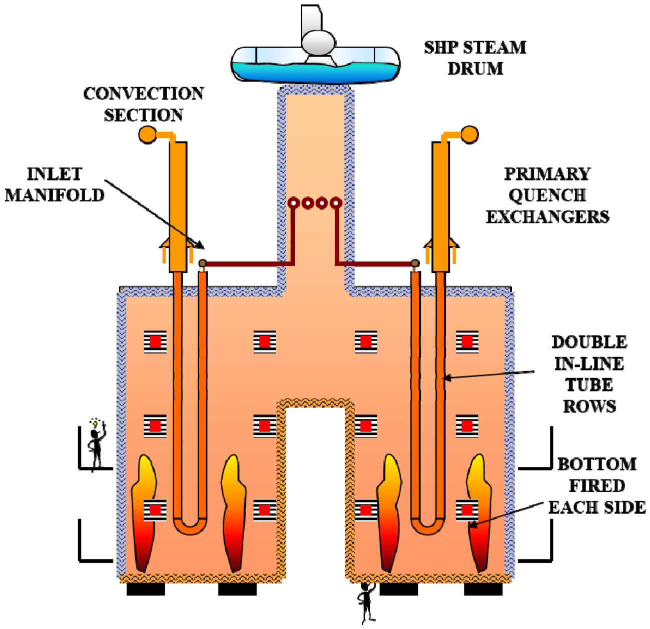

Figure 5. Typical End View Two pass

3. W sweep Bends- one or more pass of increasing size – W configuration – fire box roof to roof orientation

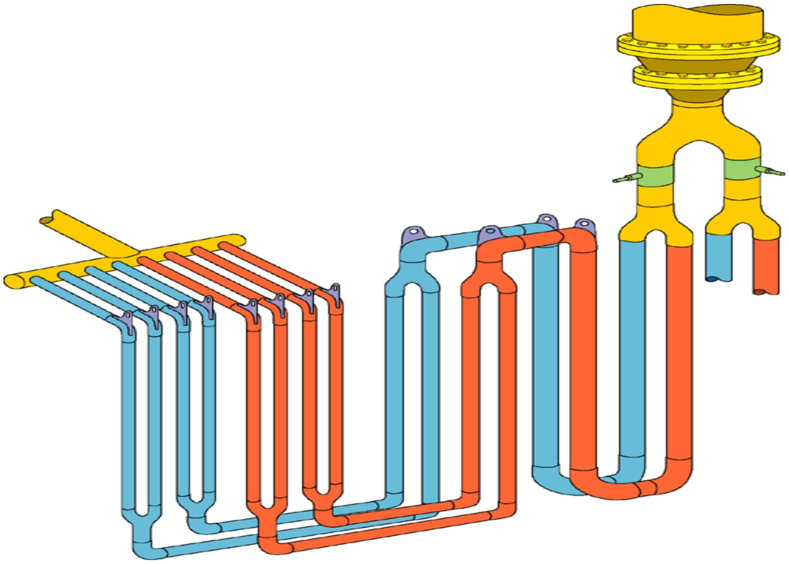

Figure 6. Coil Configuration

4. Hybrids – one or more passes of increasing size – fire box roof to roof orientation

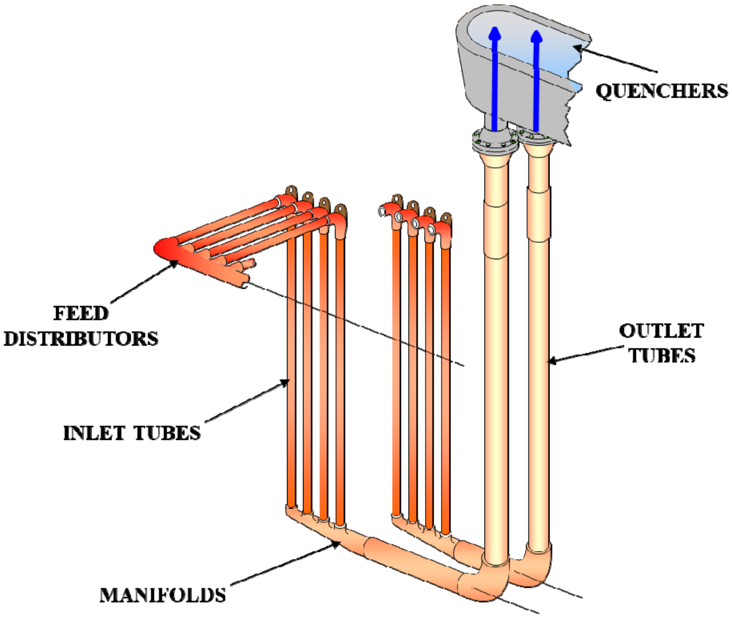

Figure 7. Coil Configuration Hybrid Coil

Table 2. Typical Residence Times by size of coil

	Size	Residence Time (seconds)	Design run Length on Naphtha	Design Decoke Time (hours)
Coil One	**1 inch by forty feet**	**0.08 - 0.12**	**30-35 Days**	**18-24**
Coil Two	**2 inch by eighty feet**	**0.20 – 0.25**	**35-45 Days**	**24-30**
Coil Three	**4 inch by 120 feet**	**0.35 – 0.45**	**45-60 Days**	**30-36**
Coil Four	**2 inch to 6 inch by 80 feet**	**0.20 - 0.25**	**35-45 Days**	**24-30**

Advantages of Coil 1

1. Highest Olefin Conversion due to short residence time
2. Down Stream Separation Section can be smaller.

Advantages Of Coil 2

1. Moderate Olefin Conversion
2. Operations Friendly
3. Dilution Steam and Feed tolerant
4. Moderate coil life
5. Moderate Thermal shock

Advantages Of Coil 3

1. Good run length between decokes
2. Good coil life
3. Moderate Thermal shock

Advantages Of Coil 4

1. Good run length between decokes
2. Good coil life
3. Good Thermal shock
4. Dilution Steam and Feed tolerant

Table 3. Typical Residence Times yields for light Naphtha

Residence Time (seconds)	0.10	0.20	0.50
Methane	15.48	15.78	16.16
Ethylene	34.16	32.16	29.37
Propylene	17.02	17.35	17.78
Butadiene	5.2	5.1	5
Benzene	5.89	6	5.75
Toluene	2.59	2.65	2.52
Fuel Oil	3.12	3.35	3.61

IMPACT OF DECOKING ON FURNACE AVAILABILITY

Non-optimal decoking results in lower availability of furnaces. In general, one in three of the ethylene plants are furnace limited, therefore improving the decoking process can increase plant utilization. In some sites, utilization improvements of several percent have been achieved by improving the decoking process.

Effects of non-optimal decoking can be as follows:

1) Increased decoking time.
2) Reduced furnace run length as a consequence of incomplete decoking.
3) Extra downtime due to extra mechanical cleaning of transfer line exchangers (TLEs).
4) Damage of coils (e.g. local bulging of coils is often caused by local overheating/carburization due to incorrect decoking procedures)

DEFINITIONS

BFW – Boiler Feed Water

Carburization – Migration (diffusion) of carbon from coke layer into alloy tube metal.

Condensation – Reactions where two or more small fragments combine to produce larger stable structures such as cyclo-di-olefins and aromatics.

CIT – Coil Inlet temperature

COT – Coil Outlet temperature

EOR – End of Run

FPH – Feed pre-heat

Hydrocracking – Decomposition by free radical chain mechanisms into the primary products: hydrogen, methane, ethylene, propylene and larger olefins.

Hydrogenation and dehydrogenation – Reactions where paraffins, di-olefins, and acetylenes are produced from olefins.

PTLE – Primary Transfer Line Exchanger

STLE – Secondary Transfer Line Exchanger

TLE – Transfer Line Exchanger

TTLE – Tertiary Transfer Line Exchanger

TMT - Tube metal temperatures are indicator when a furnace needs decoking.

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