# PYROLYSIS FURNACE

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## ABSTRACT

Pyrolysis or steam cracking is the primary process utilized to manufacture olefins from large hydrocarbon molecules. This gas-phase reaction takes place in metal alloy tubes within a fired furnace. Pyrolysis proceeds as a series of free radical reactions and the complexity of the mechanisms increases with the nature of the feedstock. Both rigorous and empirical solution techniques are available. A mathematical model for design of pyrolysis coil is presented. The effect of residence time, temperature, pressure and inert on ethylene yield will be discussed briefly.

Coke formation onto the tubular coils continues to be a challenge faced by engineers. Coke deposition increases fuel consumption, reduces the furnace throughput and causes non-productive outages for decoking activities. Various coke formation mechanisms will be discussed and a review of recent developments to mitigate this phenomenon will be presented.

*Keywords:* Coking, ethylene, furnace, olefins, pyrolysis, steam cracking

## 1 INTRODUCTION

Olefins manufacturing is the third largest petrochemical sector after ammonia manufacturing and petroleum refining. Olefins are the building blocks in manufacturing of polymers and elastomers or converted into derivatives such as aldehydes, alcohols, glycols, etc. Olefins are primarily produced by steam cracking of large hydrocarbon molecules. This process is also known as pyrolysis.

Pyrolysis is a gas-phase reaction at very high temperature. As the reaction is highly endothermic, it is carried out in tubular coils within a fired furnace. Many furnace designs are available today, although the fundamental principles are similar. Commercial technology can be licensed from technology providers e.g., Kellogg Brown & Root, ABB Lummus, Stone & Webster, Linde, KTI-Technip, etc.

An industrial pyrolysis furnace is a complicated piece of equipment that functions as both a reactor and high-pressure steam generator. The pyrolysis reactions proceeds in tubular coils made of Cr/Ni alloys. These coils are hung vertically in a firebox. Depending of furnace design, there may be between 16-128 coils per firebox. Burners are arranged on the walls and on the floor of the firebox for indirect firing. This section is called the radiant section because the radiant heat is recovered. At the end of the pyrolysis, the reaction needs to be quenched rapidly to avoid further decomposition of the desired olefins. This is achieved by either indirect cooling using a quench exchanger or direct cooling by injecting quench oil into the gas effluent. The heat carried by the flue gas is recovered at the convection section of the furnace. This section consists of a series of “tube banks” where the heat is recovered for superheating steam, preheating the hydrocarbon feed, boiler feed water and dilution steam.

Being the heart of a cracker unit, furnace technology continues to be an active area of research. The large amount of energy consumed in both the pyrolysis reaction and recovery of the products drives engineers to continuously improve the energy efficiency of the process. Higher selectivity designs helps to reduce the size of the recovery section and hence, the capital cost of a steam cracker.

## 2 PROCESS CHEMISTRY

The desired products from the pyrolysis reactions are light olefins, i.e., ethylene, propylene and butadiene. However, depending on the nature of the feedstock, a wide array of by-products can be produced as result of pyrolysis. This includes hydrogen, methane, acetylene, butene, benzene, toluene, xylene and other hydrocarbon structures up to $C_{12}$ length. A wide variety of feedstock for pyrolysis can be employed with ethane and naphtha being the most common. Other feedstocks used are propane, liquefied petroleum gas (a propane and butane mixture), kerosene, atmospheric gas oil, vacuum gas oil and wax.

The desired reaction is the decomposition of the hydrocarbon molecule (typically of paraffinic structure) to its olefinic equivalent. The simplest illustration is decomposition of ethane into an ethylene molecule, where the overall reaction is:

$$C_2H_6 \longrightarrow C_2H_4 + H_2 \tag{1}$$

The mechanism of this reaction however involves a series of free radical reactions as proposed by Rice and Herzfeld (1934). This can be divided into four steps: initiation, hydrogen abstraction, radical decomposition and termination.

Initiation

$$C_2H_6 \xrightarrow{k_1} CH_3* + CH_3* \tag{2}$$

Hydrogen abstraction

$$CH_3* + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5* \tag{3}$$

$$H* + C_2H_6 \xrightarrow{k_3} H_2 + C_2H_5* \tag{4}$$

Radical decomposition

$$C_2H_5* \xrightarrow{k_4} C_2H_4 + H* \tag{5}$$

Termination

$$H* + H* \xrightarrow{k_5} H_2 \tag{6}$$

$$H* + CH_3* \xrightarrow{k_5} CH_4 \tag{7}$$

$$H* + C_2H_5* \xrightarrow{k_5} C_2H_6 \tag{8}$$

$$C_2H_5* + CH_3* \xrightarrow{k_5} C_3H_8 \tag{9}$$

$$C_2H_5* + C_2H_5* \xrightarrow{k_5} C_4H_{10} \tag{10}$$

In pyrolysis of larger hydrocarbons, the initiation step of splitting the C-C bond can occur in variety of ways depending on the molecule structure. Addition transient chain reactions can be occurring simultaneously. In high severity condition (very high reaction temperature), the olefins produced as well as the species formed in the termination step can proceed for further decomposition.

In pyrolysis of multi-component hydrocarbon mixtures, e.g., naphtha and gas oil, the multiplicity of reactions that occurred and the largely unknown componential composition, rigorous free radical mechanism solution is difficult. Techniques of “lumping” groups of chemical species with similar kinetic behavior, similar to those utilized in catalytic cracking were developed. These techniques lump the hydrocarbon into groups of normal paraffin, iso-paraffin, olefin, naphthene and aromatic. Empirical solutions, e.g. Kivlen (1990), correlates the key components in the product to these lumped groups, as well as the specific gravity, boiling range, hydrogen content, etc. Modern modeling package, e.g., SPYRO offers a rigorous solution that combines technique of lumping components and free radical mechanism.

Two major undesired reactions that occur simultaneously with the desired cracking of alkanes are dehydrogenation and condensation. Dehydrogenation is the phenomenon where an olefin molecule further decomposes into a diolefin or the C≡C group. Examples are formation of acetylene, methyl acetylene and propadiene:

$$C_2H_4 \longrightarrow C_2H_2 + H_2 \tag{11}$$

$$C_3H_6 \longrightarrow C_3H_4 + H_2 \tag{12}$$

Dehydrogenation results in olefin yield loss. Its products are contaminant to the olefin product. In the case of acetylene, methyl acetylene and propadiene, they had to be removed downstream using palladium-based hydrogenation reactors, which are expensive and difficult to operate.

Condensation is a reaction where two or more small molecules combine to form a larger stable structure such as cyclo-diolefins and aromatic. This secondary reaction occurs in the latter stage of pyrolysis and the residence time of the reactor is high. In practice, this can be observed when the aromatic concentration in the pyrolysis gasoline (a by-product) stream and the residual fuel oil ($C_9$-$C_{12}$ fraction) are high.

The extreme of dehydrogenation and condensation is coke formation. Coke forms when hydrogen atoms are removed from the hydrocarbon radicals until the extreme of leaving only a layer of elemental carbon or coke. Although, aromatic are relatively stable molecules, they can however further react via condensation to form a chain of its benzene ring structure. These condensation products leave the gas phase and settle on the inner walls of the radiant coils as a layer of hard coke that is very difficult to remove. Various mechanism of coke formation will be discussed later in detail.

## 3 REACTOR PARAMETERS

The pyrolysis coils essentially behaves as a plug flow reactor that receives heat from its surrounding, i.e., the radiant heat of the firebox. Much of the early development of furnace technology found inspirations in the works of Schutt (1959). In industrial pyrolysis of ethane, it was found that the methane yield increases and the ethylene yield decreases with the approach to the equilibrium of ethane dehydrogenation reaction. The equilibrium approach $\varepsilon$ can be defined as:

$$\varepsilon = \frac{P}{K_p} \frac{\left(y_{H_2}\right)\left(y_{C_2H_4}\right)}{\left(y_{C_2H_6}\right)} \tag{13}$$

where $P$ = hydrocarbon partial pressure, Pa

$K_p$ = equilibrium constant for the ethane dehydrogenation reaction at the coil outlet temperature, Pa

$y$ = mole fraction of constituent in the hydrocarbon mixture of the coil effluent

Based on Schutt's data and assumption that every decomposing mole of ethane not converted to ethylene will yield 2 moles of other pyrolysis products, the molal yield of ethylene per converted mole of ethane can be represented by the following formula:

$$Y_{C_2H_4} = \frac{1.67K_p}{P}\frac{1-\alpha^2}{\alpha^2}\left(\sqrt{1+1.2\frac{P}{K_p}\frac{\alpha^2}{1-\alpha^2}}-1\right) \tag{14}$$

where $\alpha$ = fractional disappearance of ethane
$Y_{C_2H_4}$ = yield of ethylene, moles per mole of ethane converted

The formula shows that higher equilibrium constants and lower partial pressures favor ethylene formation. Higher equilibrium constants require higher reactor temperatures, which in turn result in higher reaction velocities and therefore call for shorter residence times to maintain a given conversion and thus, obtain a higher ethylene yield. This work prompted designers of pyrolysis furnaces to move in the direction of short residence time, low hydrocarbon pressures and high temperatures for optimum production of ethylene from any feedstock.

### 3.1 Residence Time

The bulk residence time, often mentioned in the literature to characterize various furnace designs, represents the entire length of time that a unit gas spends in the pyrolysis coil.

$$\theta_B = \int_0^L \frac{dl}{v(l)} \tag{15}$$

where $L$ = total coil length
$L$ = distance from the coil inlet, m
$v(l)$ = Gas velocity, ms$^{-1}$
$\theta_B$ = bulk residence time, s

However, investigators showed that it is the residence time of the pyrolysis products rather than the bulk residence time that influences the yield spectrum. Zdonik (1970) proposed an “equivalent residence time” based on the decomposition of the *n*-pentane, one of the more refractory product commonly found in the pyrolysis of liquid feedstock.

$$\theta_E = \frac{1}{K_5(\theta_B)}\int_0^{\theta_B} K_5(\theta)\,d\theta \tag{16}$$

where $\theta_E$ = equivalent residence time, s$^{-1}$
$\theta_B$ = bulk residence time, s
$K_5$ = reaction rate of n-pentane, s$^{-1}$

All the early pyrolysis cracking furnaces constructed between 1940 and 1960 had horizontal radiant tubes and residence times in excess of 0.5 seconds. Radiant tube materials were 310 stainless (wrought 25 Chrome 20 Nickel) or Incoloy with internal diameter (ID) larger than 127 mm (5-in). Until mid of 1960s’ all furnaces were fired with a very large number of wall burners spaced on about 1,829 mm (6-ft) centers in the horizontal walls and facing the row of radiant tubes.

In order to reduce the residence time, engineers have designed radiant tubes of smaller diameters, better metallurgy and burners that are more efficient. Modern cracking furnaces operate in residence time range between 0.08-0.25 s. Tube diameter has reduced to the range of 25.4 – 101.6 mm (1-4 in). The smaller diameter tubes offer a higher surface to volume ratio, which allowed the heat necessary for cracking to enter the tubes in a much shorter tube length. This enabled 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). Radiant coils are now casted with composition of Cr/Ni in the range of 25/35 to 35/45 and installed vertically to reduce the investment cost. Large wall burners were replaced with smaller but more efficient floor burners (Bowen, 1992).

| | Yield in Weight Percent | | |
|---|---|---|---|
| Residence Time | 0.10 s | 0.20 s | 0.50 s |
| Methane | 15.48 | 15.78 | 16.16 |
| Ethylene | 34.16 | 32.16 | 29.37 |
| Propylene | 17.02 | 17.35 | 17.78 |
| Butadiene | 5.20 | 5.10 | 5.00 |
| Benzene | 5.89 | 6.00 | 5.75 |
| Toluene | 2.59 | 2.65 | 2.52 |
| Fuel Oil | 3.12 | 3.35 | 3.61 |

**Table 1: Effect of Residence Time in Cracking of Typical Light Naphtha** ***(Kolmetz, et al, 2002)***

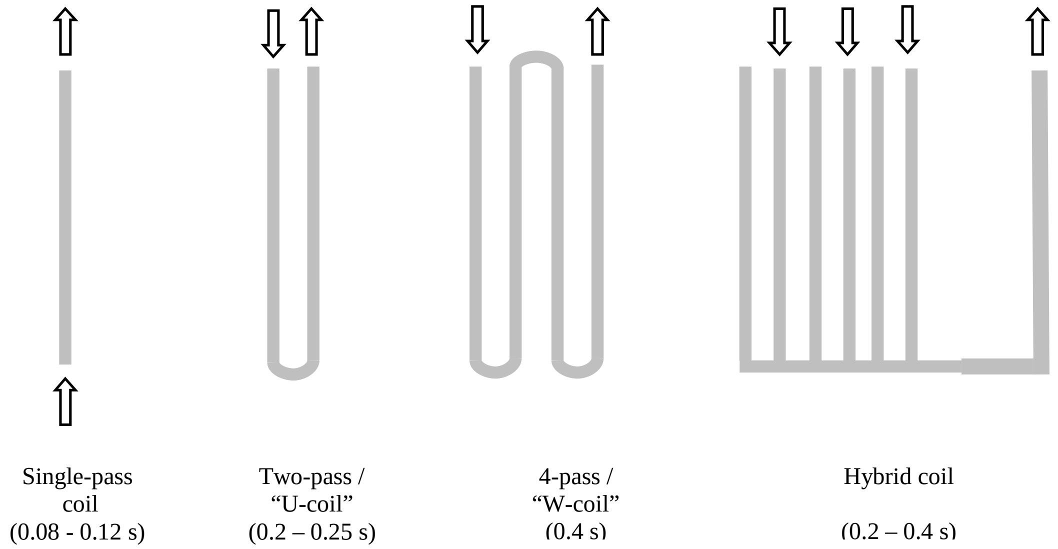

**Figure 1: Types of Coils in Industrial Pyrolysis**

## 3.2 Reaction Temperature

Pyrolysis is a highly endothermic reaction. For a given tube dimension and operating pressure, increase in reaction temperature drives the reaction to the right to produce smaller hydrocarbon molecules. Over the last few decades, the operating temperature of pyrolysis furnace has steadily been spread from the region of 750 – 850$^{o}$C to close to 900$^{o}$C.

The downside of higher operating temperature is more rapid coking rate and carburization, which shortens the tube-life. Hence, engineers have continuously worked to developed technology to suppress coke formation, better metallurgy to sustain the elevated temperatures, as well as, techniques to reduce carburization. As the initiation step of coking and carburization is the same, i.e., formation of catalytic coke, recent developments have been collaborative works of both fields of interest.

## 3.3 Reaction Pressure

Pyrolysis is a gas-phase reaction, which produces more moles of gas molecules for its reaction to the right. Hence, low operating pressure is favored. Modern furnaces operate under low pressure of 175-240 kPa. Although innovative coil design has reduced coil pressure and contributed better yields, the major credit goes to improvement in the compressor technology. The coil outlet pressure is indirectly controlled by the suction pressure of a process gas compressor located downstream.