Advances in Cracking Furnace Technology

Karl Kolmetz
karl@kolmetz.com

John Kivlen
jkivlen@bellsouth.com

Jeff Gray
jeffngray@hotmail.com

Cheah Phaik Sim
piximmink@yahoo.com

Cyron Anthony Soyza
cyronsoyza@hotmail.com

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Advances in Cracking Furnace Technology

Outline

1. Introduction
2. Historical Development
3. Design Constraints
4. Comparison of Current Designs
5. Furnace Run lengths
6. Anti Coking
7. Future Opportunities
8. Conclusions
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.
Introduction

- 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.
History

• The first commercial unit for pyrolysis cracking of hydrocarbons was commissioned at Esso’s facility in Baton Rouge, Louisiana during 1943.

• The feedstock was Gas Oil and the Butadiene extracted from the cracked products was used to make Butyl rubber.
• Ethylene, propylene and other products were flared.

• Shortly thereafter, two more commercial pyrolysis-cracking units were constructed along with ethanol and ethylene glycol plants to utilize the ethylene.
• All pyrolysis cracking furnaces constructed during the 40’s and 50’s 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. Cast tubes were not yet invented.
History

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 utilizes wall burners for a small portion of the heat fired. This change made possible because of much better control of the excess air within the firebox.
• During 1960 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.
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.
Design Constraints

• The heat transfer to the tube is effected largely by radiation and only to a small degree by convection.

• The firebox temperature is typically in the range of 1200 degrees Centigrade.
Design Constraints

1. Process Chemistry
2. Heat of Reaction
3. Metallurgy
4. Flame pattern / Fire Box
Design Constraints

Process Chemistry

• To fully understand the furnace design constraints a review of process chemistry is required.
Design Constraints

• When a hydrocarbon feedstock is undergoing pyrolysis a multitude of reactions are happening simultaneously, but for practical purposes a simplified outlook will explain many of the end results in which are of primary interest.
• Hydrocracking - Decomposition by free radical chain mechanisms into the primary products: hydrogen, methane, ethylene, propylene and larger olefins.
Design Constraints

- **Hydrogenation and dehydrogenation** – reactions where paraffins, di-olefins, and acetylenes are produced from olefins.
Design Constraints

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

Hydrocracking of Ethane

\[ C_2H_6 = CH_3^* + CH_3^* \]  (1)

\[ CH_3^* + C_2H_6 = CH_4 + C_2H_5^* \]  (2)

\[ C_2H_5^* = C_2H_4 + H^* \]  (3)

\[ H^* + C_2H_4 = H_2 + C_2H_5^* \]  (4)

\[ C_2H_6 = C_2H_4 + H_2 \]  (5)
The process chemistry review reveals at least three design requirements:

1. Low Pressure
2. Low Hydrogen Partial Pressures
3. Short Residence Time
Design Constraints

1. Low Pressure

- The predominately desired reaction is: \( \text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2 \)

- Any time the moles of products are larger than the moles of reactants, the equilibrium favors low pressures.
Design Constraints

2. Low Hydrogen Partial Pressure

• To reduce the unwanted hydrogenation reaction, lower hydrogen partial pressures would produce more of the desired products.
3. Short Residence Time

- To reduce the unwanted condensation reaction, shorter residence times would produce more of the desired products.
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.
**Design Constraints**

**Diameter To Length Ratio**

\[ Q = U A DT \]

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.
Design Constraints

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.
### Typical Metallurgy Constraints

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Composition</th>
<th>Temperature Limits</th>
<th>Developed</th>
<th>Carbon Pick Up</th>
</tr>
</thead>
<tbody>
<tr>
<td>HK 40</td>
<td>25/20 : Cr/Ni</td>
<td>1830°F 1000°C</td>
<td>Late 1960’s</td>
<td>1% at 1055°C</td>
</tr>
<tr>
<td>HP Modified</td>
<td>25/35 : Cr/Ni</td>
<td>2,060°F 1125°C</td>
<td>Early 1970’s</td>
<td>1% at 1125°C</td>
</tr>
<tr>
<td>35/45</td>
<td>35/45 : Cr/Ni</td>
<td>2100°F 1150°C</td>
<td>Mid 1980’s</td>
<td>1% at 1155°C</td>
</tr>
</tbody>
</table>
Design Constraints

Flame Pattern Constraints
Flame Pattern Constraints

- The pyrolysis reaction are endothermic and time dependant reactions.

- The flame pattern and the resulting heat flux can have the net effect of changing the effective length of the coil.
Flame Pattern Constraints

• If the heat flux is not uniform the coil effective length can be reduced.

• If heat flux is not uniform hot areas can cause over-cracking and shorting coil life.
Design Constraints

Flame Pattern Constraints

HEAT FLUX DISTRIBUTION

- Relative Heat Flux (% of Max)
- Radiant Section Height (Metres)

- Existing
- Improved
Flame Pattern Constraints

The shape of the flame is determined by burner designers according to heat input requirements by the technology provider.
Design Constraints

Flame Pattern Constraints

- The shape of the fire box will effect the flame pattern and heat flux.

- Deviation from rectangular have not proved to be successful.
Design Constraints

Flame Pattern Constraints

Fire Box Shape

- Convection Section
- SHP Steam Drum
- Primary Quench Exchangers
- Crossover Lines
- Inlet Manifold
- Double In-Line Tube Rows
- Bottom Fired Each Side
Flame Pattern Constraints

- Steam may be added to the fuel gas to reduce the NOx emissions.

- This steam has been shown to even the heat flux distribution resulting in higher yields and run lengths.
Comparison of Current Designs

• 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.
Comparison of Current Designs

- 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.
Comparison of Current Designs

Types of Furnace Coils

- SINGLE PASS
- “U”- COIL or TWO PASS
- “W”- COIL or “M” - COIL
- HYBRID COIL
Comparison of Current Designs

- 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.
Comparison of Current Designs

- For this presentation the comparison will be limited to four designs:

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

Typical End View
Single Pass

- CONVECTION SECTION
- CROSSOVER LINES
- PRIMARY QUENCH EXCHANGERS
- DOUBLE IN-LINE TUBE ROWS
- BOTTOM FIRED EACH SIDE
- INLET MANIFOLD
- SHP STEAM DRUM
2. U Sweep Bends - one or more passes of uniform size - U configuration - fire box roof to roof orientation
Comparison of Current Designs

Typical End View
Two Pass

CONVECTION SECTION
INLET MANIFOLD
PRIMARY QUENCH EXCHANGERS
DOUBLE IN-LINE TUBE ROWS
BOTTOM FIRED EACH SIDE
SHP STEAM DRUM
Comparison of Current Designs

3. W Sweep Bends - one or more pass of increasing size - W configuration - fire box roof to roof orientation
Comparison of Current Designs

Coil Configuration
4. Hybrids - one or more passes of increasing size - fire box roof to roof orientation -
Comparison of Current Designs

Coil Configuration

Hybrid Coil

- Feed Distributors
- Inlet Tubes
- Manifolds
- Outlet Tubes
- Quenchers
## Comparison of Current Designs

<table>
<thead>
<tr>
<th></th>
<th>Size</th>
<th>Residence Time (seconds)</th>
<th>Design run Length on Naphtha</th>
<th>Design Decoke Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coil One</strong></td>
<td>1 inch by forty feet</td>
<td>0.08 - 0.12</td>
<td>30-35 Days</td>
<td>18-24</td>
</tr>
<tr>
<td><strong>Coil Two</strong></td>
<td>2 inch by eighty feet</td>
<td>0.20 – 0.25</td>
<td>35-45 Days</td>
<td>24-30</td>
</tr>
<tr>
<td><strong>Coil Three</strong></td>
<td>4 inch by 120 feet</td>
<td>0.35 – 0.45</td>
<td>45-60 Days</td>
<td>30-36</td>
</tr>
<tr>
<td><strong>Coil Four</strong></td>
<td>2 inch to 6 inch by 80 feet</td>
<td>0.20 - 0.25</td>
<td>35-45 Days</td>
<td>24-30</td>
</tr>
</tbody>
</table>
## Comparison of Current Designs

### Typical Residence Times Yields for Light Naphtha

<table>
<thead>
<tr>
<th>Residence Time (seconds)</th>
<th>0.10</th>
<th>0.20</th>
<th>0.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>15.48</td>
<td>15.78</td>
<td>16.16</td>
</tr>
<tr>
<td>Ethylene</td>
<td>34.16</td>
<td>32.16</td>
<td>29.37</td>
</tr>
<tr>
<td>Propylene</td>
<td>17.02</td>
<td>17.35</td>
<td>17.78</td>
</tr>
<tr>
<td>Butadiene</td>
<td>5.2</td>
<td>5.1</td>
<td>5</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.89</td>
<td>6</td>
<td>5.75</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.59</td>
<td>2.65</td>
<td>2.52</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>3.12</td>
<td>3.35</td>
<td>3.61</td>
</tr>
</tbody>
</table>
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
4. Moderate Thermal shock
• The coke layer can reach > 10 mm thickness depending on the type of feedstock and severity.
• The thickness of the coke is a function of the TMT and conversion
Comparison of Current Designs

Thermal Shock
Comparison of Current Designs

Thermal Shock
Advantages Of Coil 3

1. Good run length between decomes
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
Comparison of Current Designs

Coil 1 Quench Exchanger

1. Established reliable system
2. Many units in operation
3. Metallurgy of Quench Exchanger is very important - Should be sodium stress corrosion resistant
Comparison of Current Designs

Typical Elevation
Single Pass

Components:
- Stack
- ID Fan
- Steam Drum
- Outlet Manifolds
- Crossover Lines
- Radiant Box
- Radiant Tube Banks
- Inlet Manifolds
- Convection Section
- Primary Quenchers
Comparison of Current Designs

Coil 2 Quench Exchanger

1. Established reliable system
2. Many units in operation
3. Metallurgy of Quench Exchanger is very important - Should be sodium stress corrosion resistant
Comparison of Current Designs

Coil 3 Quench Exchanger

1. Established reliable system
2. Many units in operation
3. Metallurgy of Quench Exchanger is very important - Should be sodium stress corrosion resistant
Comparison of Current Designs

Coil 4 Quench Exchanger

1. Recently changed system to reduce residence time
2. Metallurgy of Quench Exchanger is very important - Should be sodium stress corrosion resistant
3. Previous design required hydro blasting every 6 months
Comparison of Current Designs

Quencher
Furnace Run Lengths

- Many factors influence furnace run lengths. A partial list includes:

1. Decoke Procedure
2. Sulfiding Procedure
3. Tube size and metallurgy
4. Feed and Steam impurities
5. The ability to utilize steam only decokes
6. Use of coke mitigating additives
### Furnace Run Lengths

<table>
<thead>
<tr>
<th></th>
<th>Design run Length on Naphtha</th>
<th>Actual run length on Ethane</th>
<th>Actual run length on Naphtha</th>
<th>Cause of Deviation</th>
</tr>
</thead>
</table>
| Coil One | 30-35 Days                  | 10-20                       | 30                          | 1. Feed Impurities  
2. Dilution Steam Impurities  
3. Flame / Fire Box Issues |
| Coil Two  | 35-45 Days                  | 20-25                       | 30-35                       | 1. Over sulfiding  
2. Low air during decokes   |
| Coil Three | 45-60 Days                  | 35-40                       | 40                          |                    |
| Coil Four  | 35-45 Days                  | 30-40                       | 45-50                       | 1. Sulfiding impurities   |
Mixing Element Radiant Tube (MERT)

- Developed by KUBOTA
- Aims to create additional turbulence resulting in efficient and homogeneous heating of gas
- Efficient heating allows lower Tube Skin Temperatures and Higher yield
Mixing Element Radiant Tube (MERT)

- Properties include:
  1. Heat transfer Co-efficient increased by 20-50% compared to bare metal
  2. 2% larger surface area
  3. 3% weight gain
  4. 2.0-3.5 times higher pressure drop
Furnace Run Lengths

PEP Cast Finned tubes

[Diagram of finned tubes with labels for plain bore, external and internal heating surface, and finned surface area.]
Anti-Coking Technologies

1. GE Betz - Pycoat
2. Nalco - Cokeless
3. Chevron / Phillips
   - CCA 500
4. Westaim
5. Nova / Kubota
Coking Impact in Ethylene

Coking in Ethylene Furnace

- Reduce product yields
- Restrain cracking severity
- Increase loss of production capacity
- Increase energy consumption
- Shorten coil service life
- Increase maintenance cost
- Add operator load

Furnace Utilization, 90~95%

Worldwide Production Loss

- 5% Improvement = $1 Billion/yr
- 10% Improvement = $2 Billion/yr
Metal catalysis
Metal catalyze dehydrogenation --> Carburized / metal boosted --> Filamentous coke growth

Radical reaction
Acetylene / Butadiene etc., growth on radical active site
Types of Coke
1. GE Betz - Pycoat

Advantages

- Treated off line - no unit contamination
- Silicon Based
**GE BetzPy-COAT Concept**

- **Diffusion barrier**
  - Adherent film: enhance binding film with metal surface
  - Barrier film: prevent carbon & oxygen from penetrating

- **Decoking Film**: Gasify the remained coke (In Development)
Coated Film

Tube Metal
Ethane Furnace Designed by KBR

Description
Located in North America
Milliseccond Furnace
27 T/Hr and 70 % Conversion
160 1.3” tubes
Main Criteria for Decoking : Coil
Inlet Pressure
Original R/L : 13-15 days
PY-COAT Performance Vs. Baseline

Run length (days)

Run #

1 2 3 4 5 6 7 8 9 10

Baseline Treated

Plant Upset
Gas Furnace Designed by KBR
Test started Mid October

PY-COAT PERFORMANCE @ NORTH AMERICA

COIL PRESSURE DROP MAX

Run days

Still operating
2. Nalco - Cokeless

Advantages

• First to develop on line coating - Several generations of development
• Present generation has shown some success
• Applied on line - high furnace utilization
• Phosphorus based
TMT Profile Comparison
Tube Metal Temperature Coil 3

- 3 basecase runs average
- 4 Coke-Less runs average
- Lummus Naphtha cracker
Anti-Coking Technologies

3. Chevron Phillips CCA 500

Advantages

• Treated off line
• Tin / Silicon Based
Coil Pressure Drop
(S-C oil, Ethane Feed)

% Maximum Coil Pressure Drop

Hydrogen Sulfide
CCA 500
3. Westaim COATALLOY™

Advantages

1. Coating applied on new tubes - Furnace Utilization
2. Carbonization Resistant
MICROGRAPH OF COATALLOY™ ENGINEERED COATING SYSTEM - BEFORE SERVICE

Engineered Surface
Enrichment Pool
Diffusion Barriers
Bulk High Temperature Alloy

50 microns
COATALLOY™-1100 CASE HISTORY - FORMOSA

Typical Runs for Uncoated Furnaces

Runs 3-9 for CoatAlloy™-1100 coated Coil

Days on Line

Maximum Pressure Drop Ratio
HIGHLIGHTS OF OTHER CASE HISTORIES

- **Short Residence Time**
  - 2% increase in ethylene yield
  - 3 x run length
  - 5% increase in conversion

- **Medium Residence Time**
  - 4.5% increase in ethylene yield
  - 2 x run length
  - 8% increase in conversion

- **Long Residence Time**
  - 4% increase in ethylene yield
  - Min. Feed rate increase of approx. 8%
  - 9% increase in conversion

![Graph showing coking rate (psi rise/day) for different residence times with bars for Uncoated-Base Conversion, Coated-Base Conversion, and Coated-10% Conversion Increase.](image-url)
4. Nova / Kubota - ANK 400

Advantages

• Coating applied on new tubes - Furnace Utilization
• 400 + Run lengths
Future Opportunities

1. Better Coil Metallurgy

- Coil manufactures will continue to develop new designs with higher temperature limits
2. Better Coil Coatings

• Research is presently ongoing in ceramics and other coke resistance materials.

• Betz / SK is developing a coke filming agent that will keep the coke in gas phase reducing accumulation on the tube.
3. Catalyst Development

- Research is presently ongoing for oxidative coupling of methane to ethane and ethylene by Li/MgO catalyst at 700 degrees C.
Conclusions

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Conclusions

• Thanks for your time
• Our goal was to give an overview of the current advancements pyrolysis cracking furnaces
• Please contact us for additional information or questions