Different types of pyrolysis coil failure

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ABSTRACT

The most occurring failure mechanisms are explained for tubes, bends and outlet parts in pyrolysis coils. The first dominant failure mechanism for radiant tubes is the combined action of carburisation and creep ductility exhaustion. This results in bulging, bending and ovalisation of the tubes. The second dominant failure mechanism is brittle fracture during furnace trips, which can result in large, longitudinal cracks on many tubes.

The process technological causes will be explained for these dominant failure mechanisms. The main causes, overheating and mis-operation, can be prevented.

The metallurgical background of the combined action of carburisation and creep ductility exhaustion will be explained. Carburisation is determined by the presence of protective oxide scales, and the nickel content of the matrix. Creep ductility exhaustion is determined by the number of cycles (start/stop- and decoke cycles) and the nature (or severity) of these cycles.

The life assessment techniques and inspection strategies should take account of all relevant failure mechanisms.
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1. Macro- & microscopic description of failure mechanisms

1.1. Radiant tubes

The two main failure mechanism for radiant tube failure are:
- ductile failure caused by carburisation and ductility exhaustion; and
- brittle failure caused by thermal shock.

The ductile failure can be recognised by a bulge on the tube and a (short) longitudinal crack on top of the bulge. The crack is not longer than the bulge. In the micro-structure creep voids can be observed between matrix and carbides. Further explanation about carburisation and ductility exhaustion is given in par.2.1.
The brittle fracture can be recognised by a long longitudinal crack which “ends” in a fork-like appearance. Sometimes, the cracks result in circumferential rupture or “windows” that fall out of the tube. The cracks can be many meters long, and many times, a thick coke layer is present inside the tube. In the micro-structure can be observed that the carbides have split. This is a marked difference to the ductile fracture and can be easily recognised.

Creep elongation (also called stretching) occurs because of creep by the self weight of the tube and the coke layer present in the tube and is influenced by temperature, the load carrying cross section of the tube, and the material used. It is generally known that HP-micro types creeps less than 45/35 types. There is also a difference of the height of the firebox. In general, modern higher furnaces suffer more from stretching than older smaller furnaces.

Another failure mechanism is overheating, which results in local melting or overall melting of the tubes. Such an overheating can happen because of lack of flow, coke blockage or burner problems (flame impingement). Lack of flow can occur when inlet valves fail or in case of compressor problems.

Above 1100°C nitriding occurs at the OD of the radiant tube (flue gas side), because nitriding kinetics are faster than oxidation kinetics. The rough as-cast surface disappears and the surface becomes a smooth and glazed appearance. Also, the lack of oxygen in the flue gas plays a rôle. Under reducing conditions (many times caused by flame impingement by badly adjusted burners) this can result in severe loss of wall thickness by alternating oxidation and nitriding. The nitrides then causes spallation the oxides. As a result a thick layer of oxides (up to 10-20 cm thick !) can be found on the furnace floor. Sometimes, this is called oxide shedding.
1.2. **Bends and outlet parts**

Erosion can be observed in 90° or 180° bends or in Y-pieces. This is caused by hard coke particles during the decoking procedure (most accepted theory). Some investigators believe that this erosion is caused by coke particles, which are present during normal operation. The remedy is to modify the decoking procedure, so that the coke is gasified instead of being spalled. Second remedy is to lower the gas velocity during decoke below 200 m/s. Third remedy is to apply “internally stepped fittings”, which have been applied successfully on many occasions.

Thermowells also suffer from erosion by coke particles. Successful solutions include:

- thermowells fully made of Stellite
- rotate the thermowell at regular intervals
- apply “diamond shape” thermowells

As in the radiant tubes, carburisation also occurs in fittings (bends, Y-pieces, tetra fittings etc.). In general, such carburisation is not life limiting for the coils, because the radiant tubes will fail before the fittings do. This is because of the high wall-thickness of the fittings.

Thick-walled bends and outlet fittings (Y-piece, tetra-fittings, flanges) may suffer from carburisation and thermal fatigue. The carburised zone is brittle and already cracks at low strains. The thermal stresses during start/stop-operation and decoke cycles cause thermal fatigue at the inside of such thick-walled components. A distinct feature is that the cracks are oriented in many directions and are opened widely. Some people call this “crazy cracking” or “mud cracking” because of this marked appearance. This type of cracking is not considered to be life limiting of the component.
2. **Metallurgical background of the main failure mechanisms**

2.1. **Carburisation and ductility exhaustion**

Carburisation is the carbon enrichment and carbide formation in the tube material under influence of the presence of carbonaceous gases and high temperatures. The carburisation rate is related to the carbon activity of the gas and progresses exponentially in relation to temperature. The material and its ability to form and maintain an oxide layer is essential to prevent carburisation.

There are several mechanisms known how an oxide layer can fail:
- diffusion distance thru the de-chromised zone is too large;
- failure of the Cr-oxide layer by formation of Cr-carbide above 1050°C;
- structural defects in the oxide (cracks, formation of spinels etc.).

According to the author’s opinion the mechanism described by Ramanarayanan [ref.1] describes the degradation mechanism best, see fig. 1. It describes the process of carburisation after failure of the oxide scale.

The resistance of materials against carburisation is given by the Ni-content and the presence of Si [ref.2], which forms a silica sub-scale, see figure 2. Therefore, modern materials have a high Ni- and Cr-content and contain 1½ - 2 %Si. The most modern Cr-oxide forming material in this respect is 45Ni/35Cr-material (such as ET45 Micro). A step forward in oxidation and carburisation resistance would be an Al-oxide forming material.
Figure 1. Oxide degradation and carburisation mechanism for pyrolysis tubes according to Ramarayanan [ref.1]

Figure 2. Influence of Ni- and Si-content on carburisation resistance [ref.2]
Creep ductility exhaustion is a complex mechanism in which the creep ductility is exhausted by cyclic operation (such as: decoke stops, plant shut-downs and trips). During normal operation a coke layer is deposited at the ID of the tube. At end-of-run (EOR) such coke layers can be up to 20 mm thick. During the decoking the coke is gasified, with the purpose that the tube is clean after the decoke. However, during the change between normal operation and decoking a temperature drop occurs. Because the thermal expansion coefficient of the metal is much higher than the coefficient of the coke, the metal-tube shrinks on the “coke-tube”. Because of the high compressive strength of coke, the metal does not crush the coke. This causes high tensile stresses in the tube metal, which relax during the (on-line) decoking procedure. The strain range that occurs is proportional to the difference in thermal expansion coefficient and the temperature range according to the equation given in figure 3.

\[
\alpha_{\text{metal}} = 19 \, \mu\text{m/m/K} \\
\alpha_{\text{coke}} = 4 \, \mu\text{m/m/K} \\
\Delta \varepsilon = \Delta \alpha \cdot \Delta T
\]

Figure 3. Tube metal and coke layer during a temperature drop

During a normal decoke such a temperature drop can be 100-200°C, which causes a strain range of 0.15-0.30 % which correspond to high stress levels. During the subsequent de-coking procedure these high stresses relax because of creep. The damage mechanism is thus cyclic creep relaxation. During each cycle the tube creeps a small amount; and at end-of-life the material reaches it’s creep ductility. That is were the name “creep ductility exhaustion” comes from. The mechanism described is similar to the failure mechanism for reformer tubes [ref.3].
Tube life is thus dependent on:
- the number of de-coke cycles \( n \);
- the severity of the cycle (start/stop, on-line or off-line decoke, \( \Delta T \)) ; and
- creep parameters (temperature, material, creep rate, creep ductility).

The combination of carburisation and creep ductility exhaustion is the “normal” failure mechanism for pyrolysis tubes in ethylene plants. It results in bulges, ovalisation and sometimes, tube bending as has been described in par.1.1. Each single occurrence is relatively simple to explain, but the complete process is complex and not yet fully understood.

### 2.2. Brittle fracture caused by furnace trips

As described in the previous paragraph the metal tube shrinks on the “coke tube” during a temperature drop. During a normal decoke the temperature drop is limited to about 100-200°C. During a furnace trip such a temperature drop can be 500-1000°C. The strain during such a furnace trip is then 0.75-1.5%. This equals the rupture ductility of aged and carburised material between RT and ~600°C. Since materials tend to crack when their rupture ductility is reached ... furnace tubes also crack. Because aged and carburised furnace tube materials are brittle at these temperatures, they crack brittle by splitting the carbides and subsequently the tubes. These brittle cracks can extend for many meters.

The risk for brittle cracks is dependent upon:
- the severity of the trip ; meaning the temperature drop ;
- the thickness of the coke layer inside the tube ; thin coke layers at SOR will be crushed, but thick coke layers at EOR will not ;
- the degree of brittleness of the material, which is determined by the amounts of ageing and carburisation.
As a guideline brittle fracture occurs most frequently when the tubes are already a few years old and when the furnace is in the second half of it’s operation run. This “dangerous area” is given in the diagram below.

![Figure 4. “Dangerous area” for brittle cracks](image)

### 3. Process technological background

The underlying problem for both failure mechanisms of radiant tubes is deposition of coke at the ID of the tube. The coke deposition causes an increase of the thermal gradient over the tube wall, which results in higher tube wall temperatures. For a tube life of ~6 years in high severity cracking EOR-temperatures can be as high as 1100°C for HP-materials (such as G4852 and derivatives) and 1125°C for 45/35 materials (such as ET45 micro). At these high temperatures the materials carburise and creep harder.
Therefore, many problems are related to furnace operation. Overheating, flame impingement, nitriding, oxide shedding, reducing flue gases, erosion, and specially brittle fracture ….. they can all be prevented by proper furnace operation.

Creep elongation, carburisation, and creep ductility exhaustion ….. they can be kept within limits by proper furnace operation, proper materials choice and good design.

4. **Relation to inspection and life assessment**

In the ideal case the inspection and life assessment tools take account of the failure mechanisms involved. However, there are no such tools available yet.

It can be helpful to measure carburisation. Several companies offer traditional carburisation meters based on magnetic principles (permeability, eddy current etc.). Recently, Shell Global presented a new pulsed Eddy Current technique, which showed promising results. However, a fully carburised tube can have a remnant life of 1-2 years (if no furnace trips occur).

Dimension measurements can be helpful as well. If creep elongation (stretching) is life limiting for the furnace, it can be monitored by the position of guide tubes. In most cases creep in circumferential direction (tube swelling, bulging and ovalisation) is life limiting. Diameter measurements by simple strapping can be helpful. However, there will be tubes that fail at low ductilities and tubes that will fail at higher ductilities (up to 15% has been observed ! ). This is dependant on the type of material (HK40, HP-Nb or 45/35), but also significant scatter between the individual tubes exists.
Accelerated creep testing of ex-service material is not suited to determine the remnant life of pyrolysis coils, because the relevant failure mechanisms (combined carburisation and cyclic relaxation) can not be taken into account by a simple creep test.

For the time being, visual inspections and strapping (diameter measurements) are the best inspection tools. One should look for bulging, ovalisation and appearance (smooth vs. rough). The results obtained can be used for trending. Many operators replace tubes about 9-12 months after the first bulges and ovalities are observed.

However, significant developments are being made in modelling the relevant failure mechanisms. Also, statistical approaches are under development.
5. **Conclusions**

- The most occurring failure mechanisms are explained for tubes, bends and outlet parts in pyrolysis coils.

- The dominant failure mechanisms for radiant tubes are (a) the combined action of carburisation and creep ductility exhaustion, and (b) brittle fracture during furnace trips. The first mechanism results in bulging, bending and ovalisation of the tubes. The second mechanism results in large, longitudinal cracks.

- The metallurgical background of the combined action of carburisation and creep ductility exhaustion are explained. Carburisation is determined by the presence of protective oxide scales, and the nickel content of the matrix. Creep ductility exhaustion is determined by the number of cycles (start/stop- and decole cycles) and the nature (or severity) of these cycles.

- Other mechanisms include creep elongation (stretching), overheating, nitriding, flame impingement, oxide shedding, gases, thermal fatigue and erosion.

- Many failures are related to furnace operation. Overheating, flame impingement, nitriding, oxide shedding, reducing flue gases, erosion, and specially brittle fracture can all be prevented by proper furnace operation. Creep elongation, carburisation, and creep ductility exhaustion can be kept within limits by proper furnace operation, materials choice and good design.

- Carburisation measurements and dimensional measurements on their own have not proved to be a succesfull inspection tool. Visual inspections and diameter measurements by strapping are the best tools. Many operators replace tubes about 9-12 months after the first bulges and ovalities are observed. However, significant developments are being made in modelling the relevant failure mechanisms. Also, statistical approaches are under development.
References


about Rob Gommans

Rob Gommans was born in 1961 and holds an M.Sc. degree in materials science of the Delft University of Technology (NL) since 1987. His M.Sc.-thesis was on creep-corrosion interaction of austenitic steels.

Between 1987 and 2000 Rob Gommans worked for DSM and was involved in metallurgical investigations, and properties and behaviour of metallic materials. He is specialised in high-temperature problems and failure analysis; and mainly worked for the synthesis gas, ethylene and power plants.

Since 2000 Rob Gommans started as an independent metallurgical consultant. The company is called “Gommans Metallurgical Services” (GMS). He works for (petro)chemical plants, power plants, paper & pulp plants, turbine and boiler manufacturers, special steel makers, engineering and contracting companies, and insurance and assessor companies.

Rob Gommans has written about 15 papers on various metallurgical subjects and holds a patent on surface modification on ethylene tubes. He is also active in various technical committees, such as the Dutch Boiler Committee and the European Collaborative Creep Committee.

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