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# Simulation of Coking in Convection Section of Steam Cracker

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This work presents CFD simulations of coke formation in the tubes of the mixture over-heater in the convection section of a steam cracker. An actual industrial feed (Gas condensate) composition is used in the simulations. The spray flow (liquid droplets in the feed) entering the tubes is simulated based on Eulerian-Lagrangian approach including a species model and a multicomponent evaporation of the droplets, using ANSYS FLUENT 13.0. The tubes of the mixture over-heater makes 3 horizontal passes (11.3 m long and 0.077 m in diameter) with U-bends connecting the passes. Droplet-wall interaction like splashing, limited splashing, rebound and stick are considered. Due to these interactions some liquid is deposited on the tube wall. The liquid deposited on the tube wall undergo partial evaporation and thermal degradation to form coke based on phase separation model of Wiehe (1993). Finally, the spatial variation in coke formation in the over-heater tube is presented as a function of various outer tube wall temperatures. For outer tube wall temperatures below the boiling point of the highest boiling compound in the feed, coke formation (~ 1 mm thick in 1 month) is observed mainly at the bends. For outer tube wall temperatures above this boiling point no coke is formed in the tubes except at the bends.

## 1. Introduction

Due to the ever increasing heavy nature of crude oil, it is expected that several changes will be required in the operating protocol of a steam cracking unit, initially designed to crack lighter feeds. An already observed change is the thermal degradation of partially evaporated feed entering the mixture over-heater tubes and the subsequent coke formation in these tubes. There is at least one industrial incident known to the authors where a tube of the over-heater choked and subsequently cracked due to internal coke formation. The importance of the coking issue is also stressed by several patents for reducing coke formation in the over-heater tubes (Chandrasekharan et al., 2005; Grondman, 1983). In the presented work, the spatial variation in coke formation in the tubes of the over-heater is studied with respect to the most important operating parameter i.e. flue gas temperature.

## 2. Problem definition

De Schepper et al. (2010) calculated that about 30 % of the liquid feed remains un-evaporated in the pre-heater/ evaporator, another heat exchanger in the convection section of a steam cracker. The partially evaporated feed (30 % liquid and 70 % vapor) is mixed with the over-heated steam, coming from yet another heat exchanger in the convection section of a steam cracker, in a feed-steam mixing nozzle. The high velocity steam atomizes the liquid feed that remains non-evaporated in the nozzle, thus creating a spray flow at the entrance of the over-heater tubes. The liquid droplets flow through the

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over-heater tubes. Some get evaporated and some impinge on the tube walls. The latter results in a deposition of liquid on the over-heater tube walls where further evaporation takes place. Depending on the wall temperature and the boiling point temperature of the deposited liquid, a fraction of the liquid is vaporized and a fraction of non-volatile compounds is converted into coke. In this study the position and the amount of coke formed on the inner side of over-heater tubes is presented as a function of the outer wall temperature. The outer wall temperature is related to flue gas temperature with flue gas side heat transfer coefficient. Since flue gas side simulations are outside the scope of this work, hence the focus of the discussion is on outer wall temperature of tubes as independent variable.

### 2.1 Tube geometry and boundary conditions

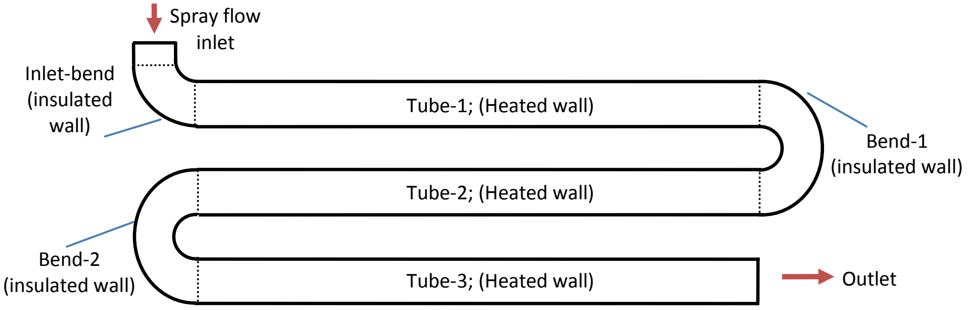


*Figure 1: Tube geometry and boundary conditions*

In present work an industrial size steam cracker, as previously discussed by De Schepper et al. (2010) is simulated. The tubes in the over-heater are 11.3 m long, 0.077 m in diameter and makes three passes (*Figure 1*). The U-bends are located outside the convection section and are insulated. The straight sections of the tubes have a tube wall thickness of 0.005 m and are subject to hot flue gases on outside. Three outer tube wall temperatures are simulated (650 K, 700 K and 750 K). The thermal resistances of the tube wall, of the coke layer (wherever formed) and of the internal fluid film are considered in simulations. Vapor (feed vapor + water vapor) feed rate at the inlet was 1.11 kg/s and relevant feed rate of droplets was 0.075 kg/s.

## 3. Numerical models

### 3.1 Flow models

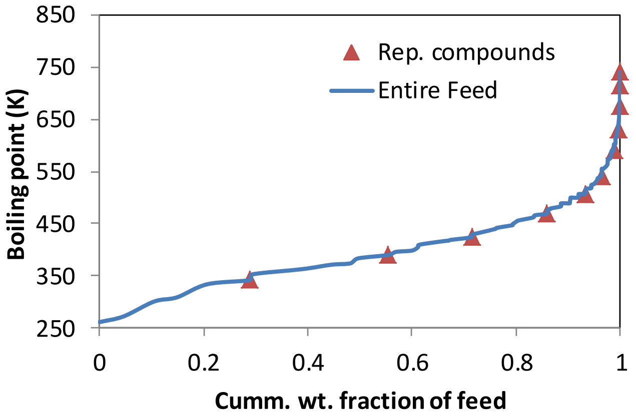


*Figure 2: Boiling point curve for the feed and representative compounds*

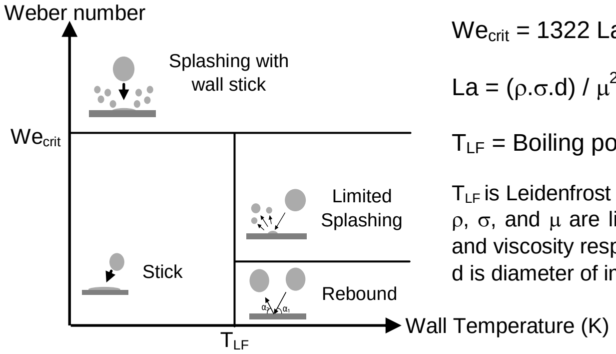
For simulating the spray flow, the Eulerian-Lagrangian approach, as available in ANSYS FLUENT 13.0, is used. The continuity equation and the Reynolds Averaged Navier-Stokes (RANS) equations are solved for the continuous phase. Standard k-$\varepsilon$ turbulence model is used to simulate turbulence in the continuous phase. Details on the above mentioned models can be found in the ANSYS FLUENT theory guide (ANSYS, 2010).

A gas chromatographic analysis of an industrial feed showed that the feed (Gas condensate) is made out of ~120 chemical compounds.. Of these 120 compounds, 11 representative compounds are selected such that they represent the entire feed in terms of boiling points. *Figure 2* presents the boiling point diagram for the entire feed and the selected representative compounds marked on it. A species transport model is used in the present work to account for the evaporation of the marked compounds from droplets to vapor, and to estimate the composition of the liquid deposited on the tube wall, as discussed later.

### 3.2 Spray flow

The velocity and position of an individual droplet is obtained by integrating the force balance over the droplet (ANSYS, 2010). The changes in the droplet mass due to evaporation of chemical compounds, the heat transfer between the droplet and the continuous phase in the tube and the droplet-wall interaction is also considered in the simulations. The mass fraction of the droplets in the inlet flow is ~12 %, equivalent to a volume fraction of ~$10^{-3}$. Thus the discrete phase, i.e. the droplets in the tube, will influence the turbulence in continuous phase (Ranade, 2002). Two way coupling between continuous phase and discrete phase is considered. As the droplets are multicomponent droplets, the evaporation rate of compounds from the droplets is based on the vapor pressure of the compounds at the droplet temperature and partial pressure of compounds in the continuous phase near the droplet (ANSYS, 2010). To ensure statistically representative results each droplet trajectory was simulated 10 times and total 2000 droplets were injected in the simulation domain.

### 3.3 Drop-wall interaction



$We_{crit} = 1322\ La^{-0.183}$

$La = (\rho.\sigma.d) / \mu^2$

$T_{LF}$ = Boiling point (K)+ 52.0

$T_{LF}$ is Leidenfrost point;
$\rho$, $\sigma$, and $\mu$ are liquid density, surface tension and viscosity respectively;
d is diameter of impinging droplet.

*Figure 3: Regime map for droplet-wall interaction*

When a droplet impinges on a tube wall it can ‘Rebound’, ‘Stick’ or ‘Splash’ into daughter droplets, depending on the Weber number of the incoming droplet, the temperature of the tube wall surface and the Leidenfrost temperature (Mills and Fry, 1982) of the droplet. The droplet behaviour is decided based on the regime map (Bai et al., 2002), modified from its original form, as shown in *Figure* 3. In the ‘Stick’ regime the droplet sticks to the wall, thus losing all its energy. The mass of the sticking droplet is added to the mass of liquid already deposited on the wall. In the ‘Rebound’ regime the droplet rebounds from the surface loosing no mass but only a small fraction of its momentum. In the ‘Limited Splashing’ regime the droplet splashes into 3 daughter droplets, while part of the droplet sticks to the wall. In the ‘Splashing’ regime the droplets breaks into several daughter droplets while only a small amount of mass sticks to the tube wall. Details on calculations of the diameter and the velocity vectors of the droplets resulting from ’Splashing’, ‘Limited splashing’ and ‘Rebound’ can be found in Bai et al. (2002), Grover and Assanis (2001), and Kandlikar and Steinke (2002) respectively.

### 3.4 Coking model

The coking model of Wiehe (1993) is used to estimate the coking rate. In a first step, the volatile fraction of the liquid deposited on the tube wall is removed by evaporation. The volatile compounds are the ones which have evaporation temperature lower than the inner temperature of the tube wall. The evaporation temperature is defined as the temperature at which the vapor pressure of the compound is one tenth of the partial pressure of the compound in the vapor phase flowing through the tube. The non-volatile fraction of the deposited liquid is split into toluene soluble compounds, heptane soluble compounds and Asphaltenes. Asphaltenes are the main pre-cursors of coke. Remark that the feed is assumed to be clean (i.e. no coke pre-cursors or Asphaltenes present in the feed, which is a rather conservative assumption). The coking reaction mechanism is given in Table 1. The reactant non-volatile heptane solubles ($H^+$) are converted into Asphaltenes cores (A*) and volatiles (V) (reaction-1). In reaction-2, the reactant Asphaltenes are converted into product non-volatile heptane solubles ($H^*$) and volatiles. The Asphaltenes cores mainly remains dissolved in the heptane soluble compounds of the deposited liquid. The excess or non-soluble Asphaltenes cores ($A_{ex}$) are then converted to Toluene insoluble (TI) solid coke as per reaction-3, which is deposited on the tube wall.

*Table 1: Coking reactions and rate constants (Wiehe, 1993)*

| **Reactions** | | **Constants** | |
|---|---|---|---|
| $H^+ \rightarrow a.A^* + (1-a).V$ | Reaction-1 | Solubility limit ($S_L$) = 0.61 (wt./wt.) | |
| $A^+ \rightarrow m.A^* + n.H^+ + (1-m-n).V$ | Reaction-2 | **Stoichiometric coefficients of reactions 1, 2 & 3** | |
| $A_{ex} \rightarrow (1-y).TI + y.H^+$ | Reaction-3 | | |
| $A_{ex} = A^* - (S_L\ (H^+ + H^*))$ | 4 | a = 0.221 | m = 0.825 |
| $TI = (1-y/(1+SL*y))*(a*Ho+(m-n*SL)*Ao)$ | 5 | n = 0.02 | y = 0.3 |

For heptane soluble non-volatiles compounds the value of the stoichiometric coefficients (a, m, n & y) for reactions 1, 2 & 3 and the solubility limit ($S_L$) are given in Table 1. The time scales of coking are of the order of 2-3 hrs. (Wiehe, 1993). i.e. in 2-3 hrs. the coking reactions in the deposited liquid should have reached a steady state in terms of coke formation. Thus the coke formation time scales are much smaller than the time scales of operation of an cracker (~months). Thus, it is assumed that the above mentioned coking reactions are instantaneous with respect to time scales of an cracker. Hence, the steady state form of the kinetic equation as shown by equation 5 in Table 1 is further used to estimate the extent of coking.

## 4. Results and Discussion

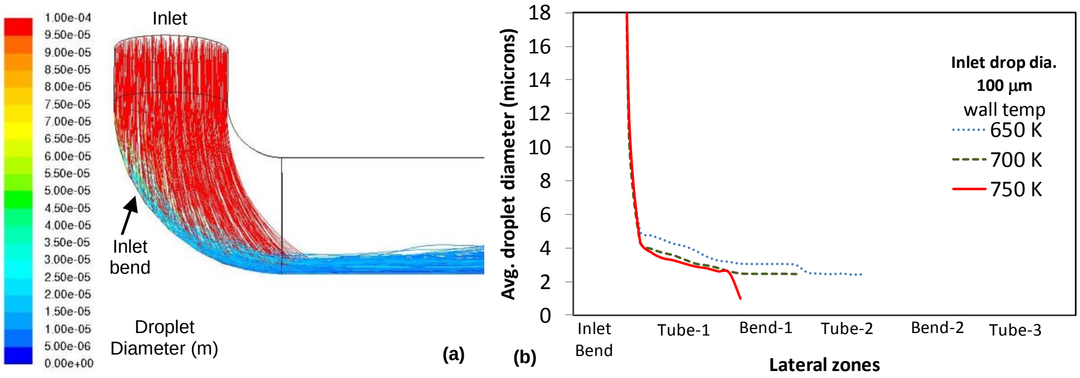


*Figure 4: Droplet trajectories coloured with droplet diameter and (b) Number-averaged droplet diameter in the tubes.*

*Figure 4a* shows trajectories of the droplets for inlet droplets with a diameter of 100 μm, in the inlet-bend of the tube. It is seen that the droplets immediately impinge the tube wall and splash into finer daughter droplets (~10 μm), which are carried along with the main flow into the straight tube section. It is observed (not shown) that for smaller droplets (1 μm) almost all droplets follow the vapor flow in the inlet-bend (limited inertial separation), resulting in a limited impingement in the inlet-bend.

From *Figure 4b* it is seen that the droplet diameter reduces from 100 μm at the inlet to 4-5 μm at the exit of inlet-bend due to impingement. After the first impingement on the tube wall in the inlet-bend, all the droplets splash into smaller droplets as their Weber number (We= 2082) exceeds the critical value ($We_{crit}$=1204). In the first tube pass the reduction of the droplet size is mainly due to (partial) evaporation of the droplets. This explains why, for higher outer wall temperatures (750 K) and thus higher temperatures of the vapor and droplets flowing through the tube, all the droplets are completely evaporated within the first tube (tube-1). In case of a lower outer wall temperature (650 K), the droplet evaporation rates are lower and the (splashed) droplets almost reach the mid-section of the second tube (tube-2). It is also observed that at bend-1 there is no noticeable reduction in droplet diameter due to droplet splashing as in inlet-bend.

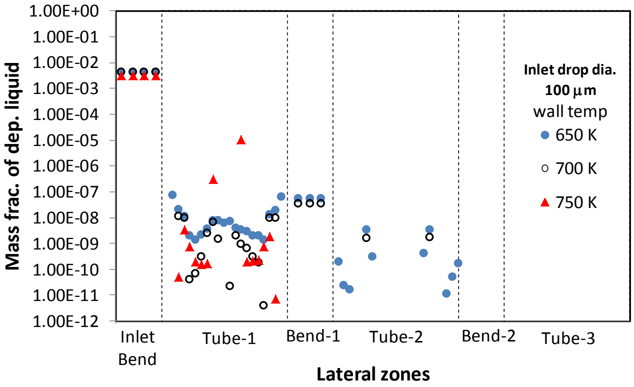


*Figure 5: Fraction of incoming liquid deposited on the over-heater tube walls*

*Figure 5* shows the fraction of incoming liquid that gets deposited in the tubes and the tube bends. As discussed, liquid deposition is observed during 'Splashing', 'Limited Splashing' or 'Stick' upon impingement on the tube wall. The highest fraction of incoming liquid is deposited in the inlet-bend, where most of the droplets splash. Finer droplets resulting from splashing easily gets carried along the tubes with the vapor flow. Smaller droplets more closely follow the vapor flow streamlines and hardly impinge on the straight tube sections. Thus, the fraction of deposited liquid in the straight tube sections is much smaller (~$10^{-7}$) as compared to the fraction in the inlet-bend (~0.005).

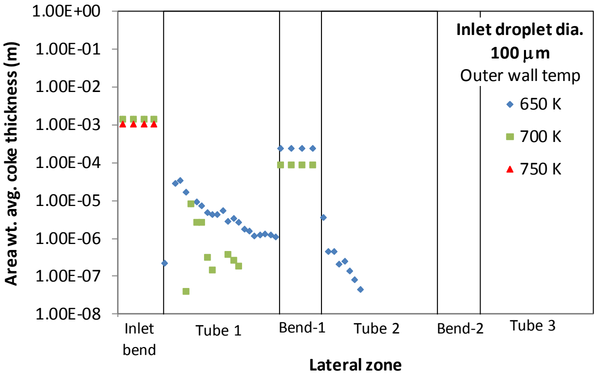


*Figure 6: Coke layer thickness formed along the tube after 30 days of operation*

*Figure 6* shows the thickness of the coke layer formed in the tube bends and the straight tube sections after 30 days of operation. It is seen that a thicker coke layer is formed in the inlet-bend and in the U-bends connecting the straight tube sections. This is as expected, as there is more liquid deposition in the bends (see *Figure 5*). It should be noted that the mass fraction of liquid deposited in the inlet-bend (0.005) is $10^4$ times higher than the liquid fraction deposited in bend-1 ($10^{-7}$), yet the coke layer thickness formed in the inlet-bend (1 mm) is only 10 time thicker than the coke layer in bend-1 (0.1 mm). This is due to the fact that the liquid deposited in inlet-bend contains more volatile compounds while the droplets which impinge in bend-1 have more of non-volatiles left after losing most of the volatiles in tube-1. For higher outer wall temperatures (750 K) coking is seen to occur only in the inlet-bend while the rest of the tube remains clean. This is due to the fact that the boiling point of the highest boiling compound (see *Figure 2*) in the feed is 740 K. Hence whatever liquid compounds deposited on the tube wall, they are volatile and evaporate back into the main tube flow. For lower outer wall temperatures (650 K) coking is observed in the inlet-bend, in tube 1, bend-1 and part of tube 2.

## 5. Conclusions

The coke formation in the tubes of the over-heater in the convection section of a steam cracker is simulated. The spray flow entering the over-heater tubes is simulated based on Eulerian-Lagrangian approach making use of a species model, multicomponent evaporating droplets, droplet-wall interaction, liquid deposition on the tube wall due to droplet impingement, removal of volatiles from the deposited liquid, coke formation from the non-volatiles in the deposited liquid and additional thermal resistance of the tube wall due to the coke layer. Overall the findings can be summarized as follows:

- The highest mass fraction of incoming liquid droplets is seen to be deposited in the inlet-bend (0.5 %) as compared to the straight tubes or other tube-bends (0.00001 %).
- There is a substantial difference in the amount of liquid deposited in the inlet-bend and in tube bend-1, but the difference in coke layer thickness between both zones is considerably smaller due to the higher volatile fraction in deposited liquid in inlet-bend.
- The coke layer thickness is higher when the outer tube wall temperature is lower than the boiling point of the highest boiling component in feed, while for an outer wall temperature above the highest boiling point of the feed no coke is formed.
- ~1 mm of coke layer is calculated to be formed in the inlet-bend and ~0.1 mm in bend-1 over a period of 1 month.

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