Simulation of Decoking of Thermal Cracking Coils by Steam/Air-Mixtures

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A rigorous approach was developed for the simulation of the decoking of an industrial cracking furnace. A one-dimensional heterogeneous reactor model, which accounts for the interfacial gradients between the process gas and the coke surface, was used to simulate reactor coils. Both the combustion and steam gasification of the coke layer were taken into account. The reactor model for the decoking was coupled with a detailed firebox simulation model. The initial profile of the coke layer thickness, required for the decoking calculations, was obtained by a run-length simulation. The evolution with time of the temperature distribution inside the cracking coil and in the furnace was generated simultaneously, which made it possible to understand the decoking operation in detail and to predict its duration accurately.

Introduction

The thermal cracking of hydrocarbons is one of the basic processes of the petrochemical industry for the production of olefins and is normally carried out in long tubular reactor coils suspended in large gas fired furnaces. In the thermal cracking of hydrocarbons, coke is deposited on the inner walls of the cracking coils by undesired side reactions. Coke formation leads to a reduction of the inner tube diameter, causing an increase of the pressure drop over the reactor which is detrimental for the ethylene selectivity. In addition, coke formation hampers the heat transfer from the firebox to the process gas inside the coils. To maintain the desired performance, the external tube skin temperature has to be increased as a function of the run time. When the pressure drop or the external tube skin temperature exceeds certain limits, the furnace has to be taken out of production to remove the coke layer by a controlled combustion by means of a mixture of steam and air. Diluted air mixtures need to be used to avoid excessive tube skin temperatures.

The decoking operation lowers the on-stream time of the firebox and implies an important loss in production capacity. Therefore, there is a strong need for accurate simulation models to optimize the decoking operation and to predict its duration.

Such a simulation model is presented in this article. Since the temperature profiles of the process gas and the external tube skin are directly affected by the heat transfer phenomena in the furnace, the simulation of the reactor coils and the firebox should be coupled to provide accurate and detailed information on the evolution of the decoking process with time. For the reactor coil simulation, use was made of a 1-D heterogeneous model, accounting for the interfacial gradients between the coke surface and the process gas. For the simulation of the heat transfer in the cracking furnace, Vercammen and Froment (1978, 1980), Rao et al. (1988), and Plehiers and Froment (1989) developed a flexible package of simulation programs, based on the zone method first introduced by Hottel and Sarofim (1967) to describe the radiative and convective heat transfer in the furnace.

The simulation package for the decoking can be used to simulate any given type of furnace configuration (such as millisecond and split coil). It can be applied as a guide for the adaptation of the operating conditions of the decoking aiming at reducing the run length of the furnace while keeping the external tube skin temperature within limits. In this article, simulation results are given for the decoking of an industrial ethane cracking furnace with a single row of vertical tubes.

Kinetic Equations

During the decoking of thermal cracking coils by a controlled combustion with a mixture of steam and air, the coke layer is assumed to react with oxygen and steam according to the following heterogeneous reactions:

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$$C(s) + O_2(g) \rightleftharpoons CO_2(g) \quad (-\Delta H^{\circ}_{298.15}) = 393.5\,\text{kJ/mol} \quad (1)$$

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad (-\Delta H^{\circ}_{298.15}) = -110.5\,\text{kJ/mol} \quad (2)$$

The gasification of the coke layer by carbon dioxide or hydrogen was not accounted for since it is significantly slower than the combustion by oxygen and the gasification by steam. The homogeneous water gas shift reaction was found to be negligible. High steam dilutions are used during the decoking. The influence of the water gas shift reaction on the partial pressure profile of steam is negligible since only small amounts of hydrogen and carbon monoxide are produced by the slow steam gasification. Furthermore, the water gas shift reaction does not affect the simulated temperature profiles since the exothermic effect of this reaction is much smaller than that of the combustion.

Duisters and Van Hardeveld (1993) studied the intrinsic kinetics of the combustion of the coke deposit (Eq. 1) in an electrobalance reactor and derived the following rate equation:

$$r_{O_2} = r_{O_2}\left[(P_{O_2})_s^s, T_s^s\right] = 180{,}336 \exp\left(-\frac{188{,}800}{RT_s^s}\right)\sqrt{(P_{O_2})_s^s} \quad (3)$$

The rate of disappearance of oxygen was found to depend on the partial pressure of oxygen and on the temperature at the coke surface.

The steam gasification of coke samples from a thermal cracking unit was studied by Bennet and Price (1982) who derived the following kinetic equation

$$r_{H_2O} = r_{H_2O}\left[(P_{H_2O})_s^s, T_s^s\right] = 50{,}925 \exp\left(-\frac{238{,}260}{RT_s^s}\right)(P_{H_2O})_s^s \quad (4)$$

The rate of steam gasification was found to be proportional to the partial pressure of steam, in agreement with the observations of Johnson (1979).

Model Equations for the Reactor Coils and for the Furnace

Reactor model

Since the decoking of thermal cracking coils is a very rapid process, involving important heat effects, the reactor model has to distinguish between the conditions in the process gas and those at the coke surface. Therefore, a 1-D heterogeneous reactor model with plug flow and accounting for interfacial gradients was developed (Froment and Bischoff, 1990). Furthermore, nonsteady-state equations need to be set up to account for the transient character of the decoking operation. Indeed, since the gas phase is depleted in oxygen, the combustion reaction is confined to a zone that gradually moves through the reactor coil as the coke layer is converted. The coke layer was supposed to be impervious for the reactants and the products because of its low porosity.

The continuity equations for oxygen and steam in the gas phase may be written

$$\frac{G}{M_m P_t}\left(\frac{\partial P_{O_2}}{\partial z} + \frac{\rho_g}{G}\frac{\partial P_{O_2}}{\partial t}\right) = (k_g)_{O_2} a_v\left[(P_{O_2})_s^s - P_{O_2}\right] \quad (5)$$

$$\frac{G}{M_m P_t}\left(\frac{\partial P_{H_2O}}{\partial z} + \frac{\rho_g}{G}\frac{\partial P_{H_2O}}{\partial t}\right) = (k_g)_{H_2O} a_v\left[(P_{H_2O})_s^s - P_{H_2O}\right] \quad (6)$$

and the energy equation for the gas phase

$$G c_p\left(\frac{\partial T}{\partial z} + \frac{\rho_g}{G}\frac{\partial T}{\partial t}\right) = h_f a_v (T_s^s - T) \quad (7)$$

The total mass flux G of the process gas ($\text{kg/m}_r^2 \cdot \text{s}$) in the coil is adjusted in each increment of the reactor accounting for the solid carbon entering the gas phase by the reactions 1 and 2.

The continuity equations for oxygen and steam at the coke surface are

$$(k_g)_{O_2} a_v\left[P_{O_2} - (P_{O_2})_s^s\right] = a_v r_{O_2}\left[(P_{O_2})_s^s, T_s^s\right] \quad (8)$$

$$(k_g)_{H_2O} a_v\left[P_{H_2O} - (P_{H_2O})_s^s\right] = a_v r_{H_2O}\left[(P_{H_2O})_s^s, T_s^s\right] \quad (9)$$

The accumulation of oxygen and steam in the coke layer is assumed to be negligible, so that a transient term is not required in these equations.

The energy equation for the coke layer is

$$a_v\left[r_{O_2}(-\Delta H)_{O_2} + r_{H_2O}(-\Delta H)_{H_2O} + Q(z)\right] = h_f a_v (T_s^s - T) + \rho_c \frac{(d_i^2 - d_r^2)}{d_r^2} c_{p_c} \frac{\partial T_s^s}{\partial t} \quad (10)$$

whereby it is assumed that the coke layer at a given position has a uniform temperature T_s^s.

The profile of the heat flux $Q(z)$ from the flue gas in the furnace to the process gas inside the coils was calculated by means of a detailed firebox simulation model, developed at the Laboratorium voor Petrochemische Techniek (Rao et al., 1988; Plehiers and Froment, 1989).

The pressure drop equation is

$$-\frac{dP_t}{dz} = F_r \frac{G^2}{\rho_g} + G\frac{du}{dz} \quad (11)$$

with

$$F_r = 0.092\frac{Re^{-0.2}}{d_r} \quad (12)$$

for the straight parts of the reactor tubes, and

$$F_r = 0.092\frac{Re^{-0.2}}{d_r} + \frac{\xi}{\pi r_b} \quad (13)$$

for the tube bends, where

$$\xi = 0.7\left(1+\frac{\Lambda}{\pi}\right)\left(0.051+0.19\frac{d_r}{r_b}\right) \tag{14}$$

(viz. Froment and Bischoff, 1990).

The initial and boundary conditions are

$$\begin{aligned} t = 0^-, z \geq 0:\ & P_{O_2} = (P_{O_2})_s^s = 0 \\ & P_{H_2O} = (P_{H_2O})_s^s = 0 \\ & T = T_s^s = T_r \\ & d_c = d_c^{\circ} \end{aligned} \tag{15}$$

$$\begin{aligned} t \geq 0^+, z = 0:\ & T = T_0 \\ & P_{O_2} = P_{O_2}^0 \\ & P_{H_2O} = P_{H_2O}^0 \\ & P_t = P_t^0 \end{aligned} \tag{16}$$

Since the partial differential Eqs. 5–7 are of the parabolic type, they can be reduced to ordinary differential equations by the method of the characteristics (Hatcher et al., 1978).

Furnace model

The decoking simulation model, describing the heat and mass transfer and reaction taking place inside the reactor tubes, was coupled with a furnace simulation model that generates a heat flux profile towards the process gas. The firebox calculations were discussed in detail by Rao et al. (1988) and Plehiers and Froment (1989) and are based on the zone method first introduced by Hottel and Sarofim (1967). In the zone method, the furnace is divided into a number of surface and volume elements with uniform properties by means of planes parallel to the furnace walls. An energy balance, containing contributions of radiative and convective heat transfer, is constructed for each element, resulting in a set of nonlinear algebraic equations. In a furnace with n surface elements and m gas volumes, the energy balance for the zone Z_i may be written

$$\sum_{j=1}^{m+n} Z_jZ_iW_{Z_j} - \sum_{j=1}^{m+n} Z_iZ_jW_{Z_i} = Q_iA_i \tag{17}$$

Z_iZ_j represents the total exchange area between the zones Z_i and Z_j. It is obtained as the ratio of the radiative energy emitted by the zone Z_i and absorbed, both directly and after reflection on other zones, by the zone Z_j to the black body emissive power WZ_i. The emissive power of a black body with temperature T_i is given by the Stefan-Boltzmann law $WZ_i = \sigma T_i^4$. The nonradiative heat flux emitted by the zone Z_i is represented by Q_i. The solution of the set of energy Eqs. 17 yields the heat flux profile towards the process gas and the temperature distribution in the furnace.

Outline of the Calculations

The initial profile of the coke layer thickness $d_c^0(z)$, required for the decoking simulations, was calculated by means of a production run length simulation. The iterative calculation procedure was discussed in detail by Plehiers et al. (1990). A 1-D plug-flow model was used to simulate the thermal cracking reactor. The cracking kinetics are based on a detailed radical reaction scheme (Willems and Froment, 1988). The profile of the heat flux between the furnace gas and the process gas was generated by the furnace model. For the integration of the continuity equation for coke, the run time was incremented in discrete steps. Use was made of the incremental pseudo steady-state approximation: in other words, the coking rate was assumed to be constant in each time interval. Time intervals of 120 h were used. A complete set of industrial data of the cracking production cycle was available. In total, 240 h of CPU time were required on an IBM RISC 6000 (model 375) computer to carry out the complete run length simulation.

After the calculation of the initial profile of the coke layer thickness, the decoking operation can be simulated. Predicting the duration of the decoking operation requires the integration of the model equations for the reactor coils and for the furnace. The calculation approach for the decoking is analogous to the one used for the production run length simulation. The decoking rate and the process conditions were considered to remain constant in each increment of time. As a consequence, the time interval Δt should be chosen sufficiently small since the temperature and partial pressure profiles change very rapidly with time. On the other hand, the firebox calculations require a considerable amount of calculation time. If a time increment of 2 h was chosen, the complete decoking simulation required 480 h of CPU time. For each increment of time, the set of partial differential and algebraic equations, formed by Eqs. 5–11 and 17, was solved together with the appropriate initial and boundary conditions, yielding the temperature and partial pressure profiles of the different components in the process gas and at the coke surface. From the corresponding decoking rate profile, a new profile of the coke layer thickness at time $t + \Delta t$ could be determined. This new profile was then used as the initial profile for the next time increment.

Simulation of the Decoking of an Ethane Cracking Furnace with a Single Row of Coils

Furnace characteristics

The simulation of the decoking operation is illustrated for an industrial ethane cracking furnace, containing four parallel reactor coils on a single row in the middle of the firebox. The reactor coils are of the swaged coil type. Each coil is 100 m long and contains eight passes. For symmetry reasons and to save computer time, only half of the furnace (2 coils) was simulated. Figures 1 and 2 show a front and a top view of half of the furnace. The main dimensions of the ethane furnace are given in Table 1.

The furnace is heated by 128 burners positioned in eight rows of eight burners in the front (A) and rear (C) wall of the furnace. During the production cycle heat is uniformly distributed over the 128 burners. During the decoking operation only 48 burners are fired. The burners of the bottom six rows are alternatively on and off, those of the two top rows are completely off. The operating conditions for the run length and for the decoking simulation are summarized in Table 2.

For the firebox calculations, the furnace is divided into zones by means of 9 nonequidistant horizontal planes, as shown in Figure 1. The decoking operation is very exothermic, resulting in negative heat fluxes to the process gas, especially in the last part of the reactor coils. If only one gas volume in the length direction is considered, the heat fluxes to the different external tube skin zones of that gas volume may not have the same sign, causing serious problems of convergence when solving the energy balances for the different zones of the firebox. Therefore, the furnace was further divided in the length direction by means of three vertical planes. The discretization of the furnace into zones results in 40 gas volumes, 160 external tube skin zones, and 68 furnace wall zones, so that the total number of zones equals 268.

Calculation of the initial profile of the coke layer thickness: run length simulation

The evolution with time of the heat flux profile during the production cycle is shown in Figure 3. The heat flux is based on the external diameter of the coil. The maximum heat flux is reached in the first bend of the coil and amounts to 115 kW/m^2. The peaks in the heat flux profile correspond to the bottom of the firebox and the valleys to the top, where the flue-gas temperature reaches its lowest values. The heat flux increases with the run time in the first two passes of the coil. This compensates for the decrease of the heat flux in the second part of the reactor coil, caused by coke formation. Coke formation results in an additional resistance to heat transfer and, therefore, in a decrease of the heat transfer to the process gas and an increase of the flue gas temperature. An increase of the average flue gas temperature at the exit of the radiation section of 30°C over the total run length was simulated.

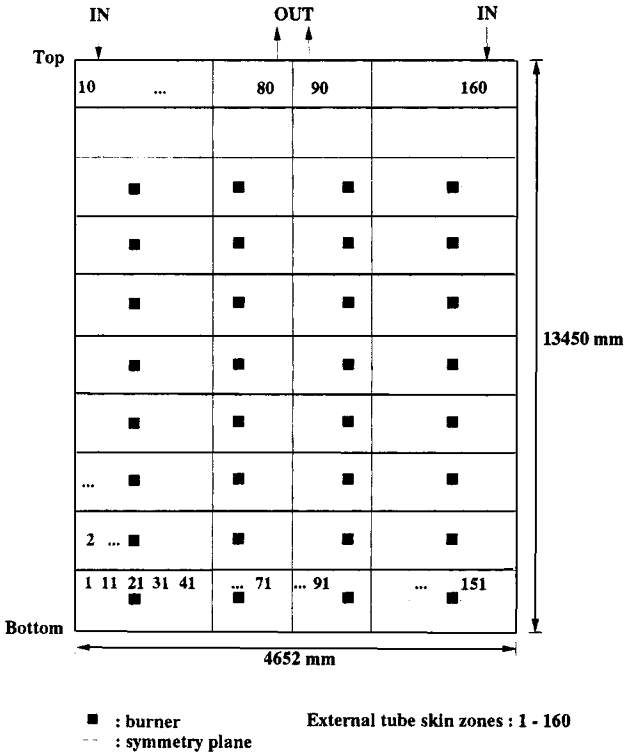

Figure 1. Front view of the ethane furnace.

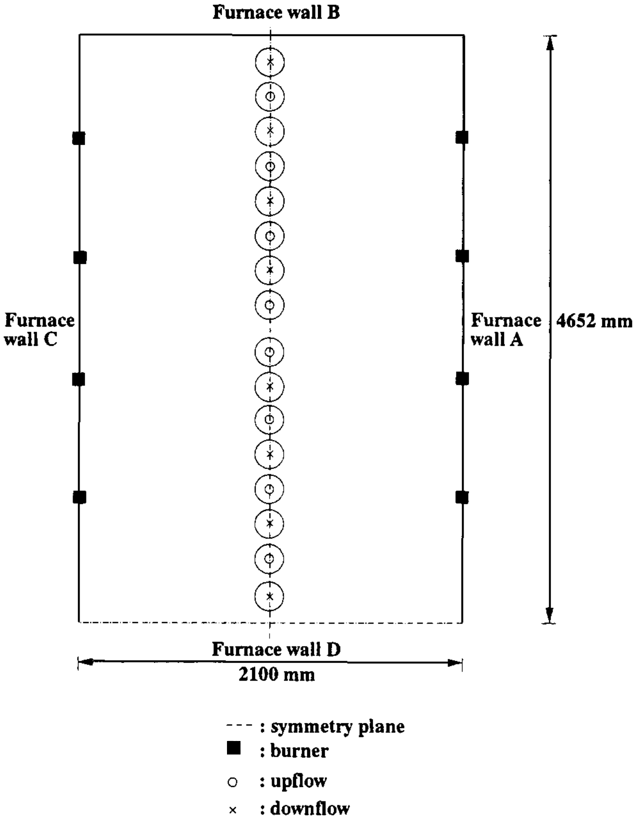

Figure 2. Top view of the ethane furnace.

Table 1. Characteristics of the Ethane Furnace

Furnace	
Length	9,304 mm
Height	13,450 mm
Width	2,100 mm
Refractory thickness	230 mm
Insulation thickness	50 mm
No. of side wall burners	128
4 coils on a single row	
Reactor Coils	
Type	Swaged coils
No. of passes of one coil	8
Total coil length	100,960 mm
Internal diameter	
passes 1–6	124 mm
passes 7–8	136 mm
External diameter	
passes 1–6	140 mm
passes 7–8	152 mm
Wall thickness	8 mm
Material Properties	
Emissivity of the furnace wall	0.6
Emissivity of the tubes	0.95
Thermal conductivity	
refractory (W/m·K)	$0.0193+118\times10^{-6}T$(K)
insulation (W/m·K)	$0.0452+111\times10^{-6}T$(K)
tubes (W/m·K)	$-8.4320+3.04\times10^{-2}T$(K)

Table 2. Operating Conditions for Run Length and Decoking Simulation

Firing Conditions	
Fuel gas composition	
Nitrogen	0.71 mol %
Hydrogen	0.5 mol %
Carbon dioxide	0.28 mol %
Methane	96.27 mol %
Ethane	0.93 mol %
Ethylene	0.77 mol %
Propane	0.82 mol %
Propylene	0.03 mol %
n-Butane	0.095 mol %
i-Butene	0.095 mol %
Run length simulation	
Initial fuel gas flow rate	2,100 kg/h
Air excess	2%
Decoking simulation	
Initial fuel gas flow rate	500 kg/h
Air excess	89%
Reactor coils	
Coil inlet temperature	620°C
Coil outlet pressure	1.7 bar
Run length simulation	
Feedstock	Ethane/Propane
Hydrocarbon feed rate per coil	3,500 kg/h
Steam dilution	0.35 – 0.4 kg steam/kg feed
Decoking simulation	
Air flow rate per coil	140 kg/h
Steam dilution	15 kg steam/kg air

The temperature at the coke surface, presented in Figure 4, follows the variation of the heat flux to the process gas. The peaks in the temperature profiles correspond to the bottom of the firebox, and the valleys correspond to the top. The temperature at the coke surface increases with time in the first part of the reactor coil because of the higher heat flux and decreases with time in the last passes of the coil due to coke formation. Since coke is deposited at the temperature of the coke surface, the simulated coking rate and coke layer thickness are strongly influenced by the coke temperature. Figure 5 shows the simulated profiles of the coke layer thickness at various times. The amount of coke, deposited near the coil inlet, is negligible. The maximum thickness of the coke layer is reached in the last bend of the coil at the bottom and amounts to 11 mm after 48 days of operation. The total amount of coke deposited in the coils equals 210 kg, in agreement with the industrial observations. CO_2-measurements during the decoking operation led to a value of 200 kg coke. Measurements of the coke layer thickness profile are impossible to obtain from the industrial production plant, unless a cracking coil blocks or cracks. The simulated run length of 48 days, based upon the limiting external tube skin temperature of 1,050°C, is in excellent agreement with the actual run length of the industrial furnace, which was 50 days. The simulated ethane conversion and coil outlet temperature amount to 54.8% and 831°C, respectively, both in excellent agreement with the plant values of 55% and 829°C. The simulated ethylene yield of 45.27% also coincides with the measured value of 45%. The maximum external tube skin temperature simulated evolves from 960°C at the beginning to 1,050°C at the end of the production run, in agreement with the plant data.

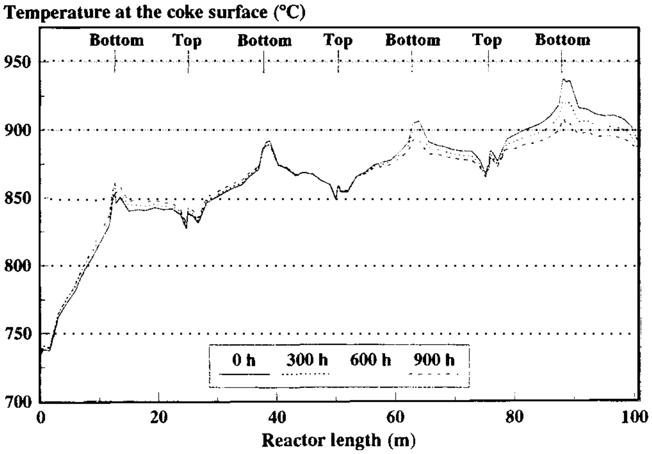

Figure 4. Evolution of the temperature profile at the coke surface with time (production cycle).

Decoking simulation: results and discussion

The decoking is determined to a large extent by the heat flux profile towards the process gas. Since this profile de-

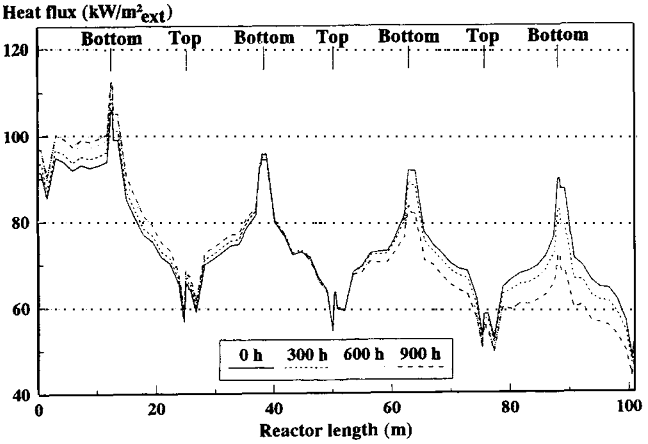

Figure 3. Evolution with time of the heat flux profile (production cycle).

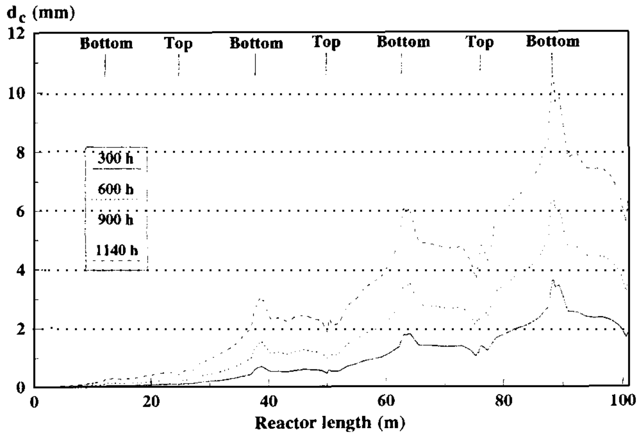

Figure 5. Evolution with time of the profile of the coke layer thickness (production cycle).

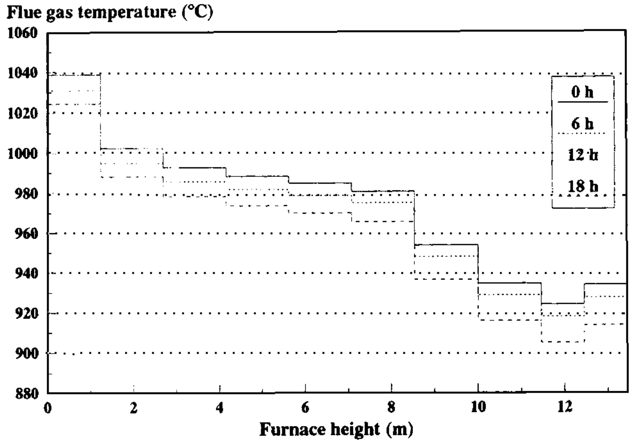

Figure 6. Profiles of the average flue-gas temperature at various times during the decoking.

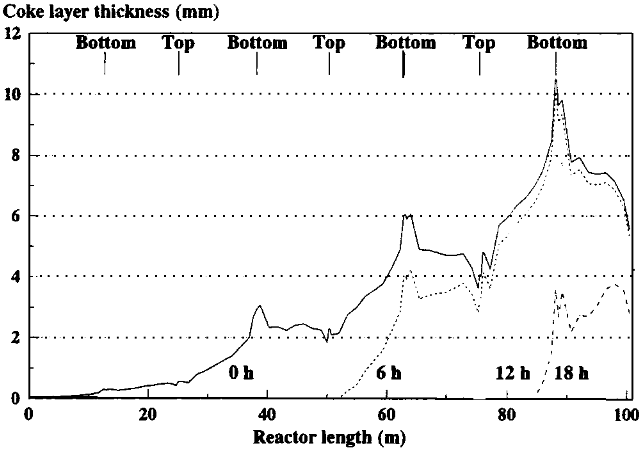

Figure 8. Evolution with time of the profile of the coke layer thickness.

pends on the conditions in the furnace, the flue gas temperature and heat flux profiles are considered first.

The evolution with time of the flue gas temperature profile is presented in Figure 6. The flue gas temperature at the bottom of the furnace is approximately 110°C higher than at the top. The flue gas temperature decreases continuously as a function of the furnace height, except near the top of the firebox. Since an important amount of heat is produced in the reactor coils by the exothermic combustion process and since no flue gas is supplied near the top of the firebox, the temperature of the external tube skin may be higher than the flue gas temperature. As a consequence, heat may be transferred from the reactor coil to the flue gas.

The nonuniformity of the flue gas temperature in the furnace results in pronounced variations in the local heat flux towards the process gas, as illustrated in Figure 7. The heat fluxes are based upon the external surface of the reactor coil and vary between 34 and -10 kW/m$^2_{ext}$. The maximum heat flux is reached in the first bend of the coil, and the minimum is reached in the sixth. The peaks correspond to the bottom of the furnace, where the flue gas temperature reaches its highest values. The valleys correspond to the top of the firebox. Due to the exothermic combustion reaction (Eq. 1), the temperature at the coke surface and at the external tube skin increase as a function of the reactor length, resulting in a decrease of the heat flux. In the last part of the reactor coil, near the top of the firebox, the heat flux becomes negative. At the upstream edge of the coke layer, the heat flux profiles were found to drop below the profile corresponding to the start of the decoking operation.

The evolution with time of the profile of the coke layer thickness is shown in Figure 8. The coke deposit is completely removed after approximately 22 h, in complete agreement with the actual decoking time of the industrial furnace.

The evolution with time of the external tube skin temperature profile is presented in Figure 9. The external tube skin temperature follows the variations of the heat flux. An important increase in temperature, varying between 10 and 30°C, occurs at the upstream edge of the coke layer, due to the exothermic combustion process. The maximum external tube skin temperature is reached in the last bend of the coil and amounts to 910°C. The simulated values for the maximum external tube skin temperature are in good agreement with the measured values of 905°C. These maximum values are

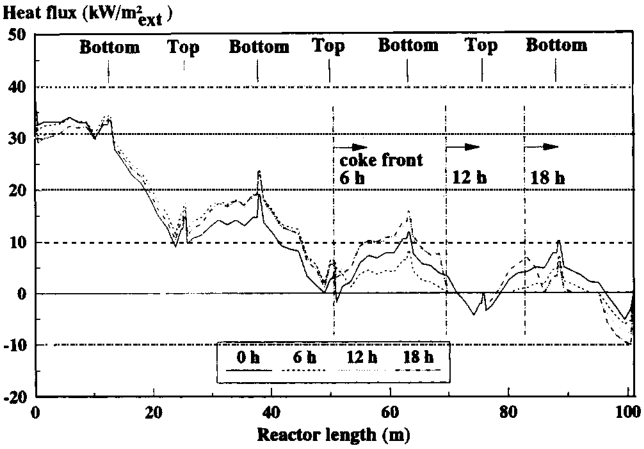

Figure 7. Heat flux profiles at various times during the decoking.

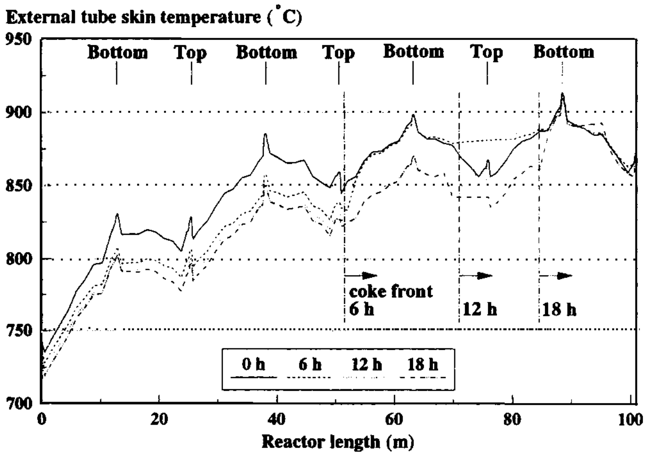

Figure 9. External tube skin temperature profiles at various times during the decoking.

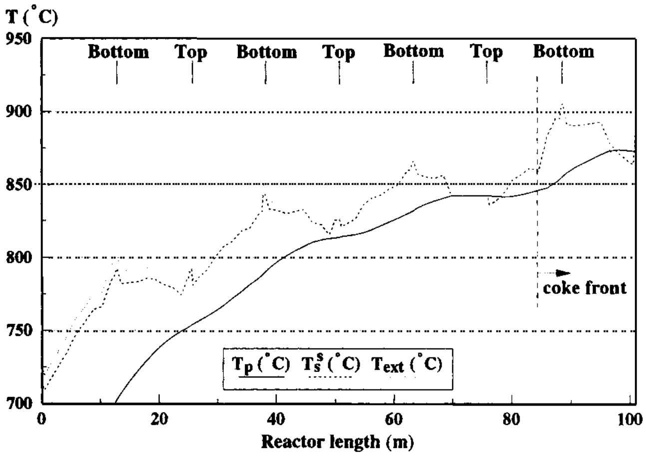

Figure 10. Temperature profiles after 18 h of decoking.

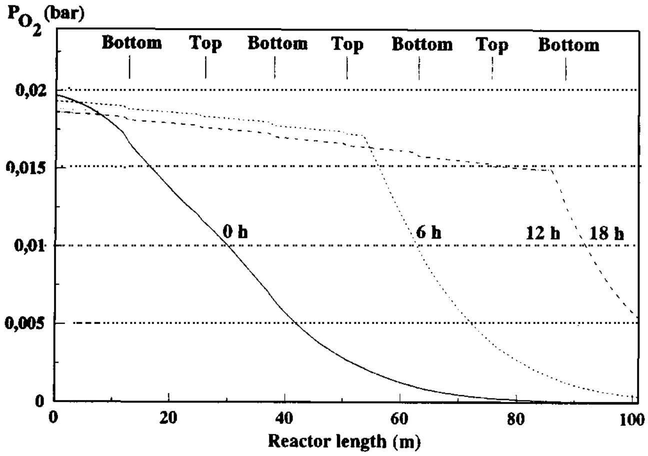

Figure 12. Time evolution of the partial pressure profile of oxygen in the process gas.

substantially lower than the limit tube skin temperature of 1,050°C, imposed by the tube material.

Differences between the temperature of the external tube skin, the coke surface, and the process gas, calculated after 18 h of decoking, are presented in Figure 10, which confirms the need for a reactor model accounting for interfacial temperature gradients. The temperature profile at the coke surface is very similar to that of the external tube skin. Because of the important resistance to heat transfer caused by the coke layer, the temperature peaks at the coke surface were found to be less pronounced than those at the external tube skin. The temperature profile of the process gas is relatively insensitive to heat flux variations. The simulated coil outlet temperature equals 880°C, in good agreement with the measured plant value of 870°C.

The evolution with time of the partial pressure profile of oxygen at the coke surface is shown in Figure 11. An important drop in the partial pressure of oxygen at the coke surface is observed at the upstream edge of the coke layer. This drop is more pronounced near the end of the decoking than at the start. At the early stages of the decoking operation, the overall rate of the combustion process is almost completely determined by the intrinsic rate of the surface reaction (Eq. 1), due to the low surface temperatures near the coil inlet. As a consequence, the global combustion process consisting of the consecutive steps of diffusion and reaction is almost completely reaction controlled and the drop in partial pressure of oxygen is small. The combustion reaction takes place in a broad zone of the reactor coil. As the reaction zone moves further down the reactor coil, the surface temperature increases. The intrinsic rate of the combustion reaction increases more rapidly with temperature than the mass-transfer rate of oxygen, so that the overall rate of the combustion process is more strongly influenced by the latter phenomenon. The global combustion process now becomes diffusion controlled, and the drop in partial pressure of oxygen increases. The amount of oxygen available at the coke surface for reaction is rapidly depleted, so that the combustion is confined to a narrow zone, gradually moving through the reactor coil as the coke layer is removed. The amount of oxygen consumed by the reaction becomes small, so that the partial pressure of oxygen in the process gas at the coil outlet increases very rapidly with decoking time (Figure 12).

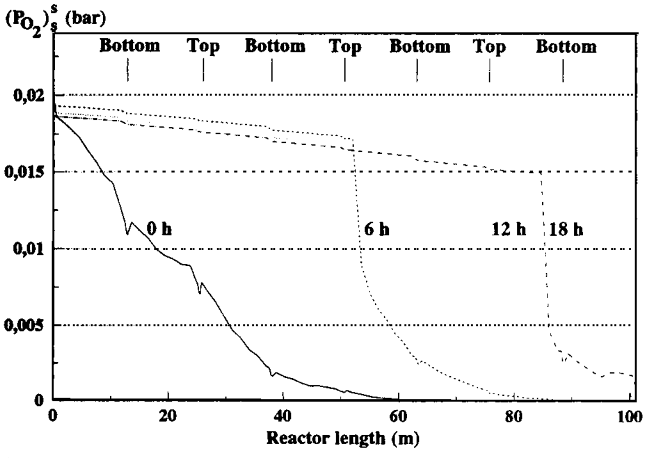

Figure 11. Evolution with time of the partial pressure profile of oxygen at the coke surface.

After 12 h of decoking, a peak in the partial pressure of oxygen at a distance of 75 m in the reactor is simulated. Since the coke is completely removed at this position, the partial pressure of oxygen at the coke surface equals that in the process gas.

The partial pressure profiles of steam at the coke surface and in the process gas are shown in Figure 13. The partial pressure of steam at the coke surface and in the process gas decreases continuously with the reactor length. Clearly, the overall rate of the gasification process is completely determined by the intrinsic rate of the reaction (Eq. 2), since no interfacial gradients of steam partial pressure occur. The global phenomenon, consisting of the consecutive steps of reaction and diffusion, is always reaction controlled, even at high surface temperatures.

Figures 11 and 13 illustrate that the decoking time can be further reduced. In the first place, the fuel gas flow rate per burner or the firing pattern can be modified, resulting in an increase of the external tube skin temperature. This leads to an enhancement of the steam gasification but does not significantly affect the combustion, due to the strong diffusion limitations involved in this reaction. The maximum tube skin

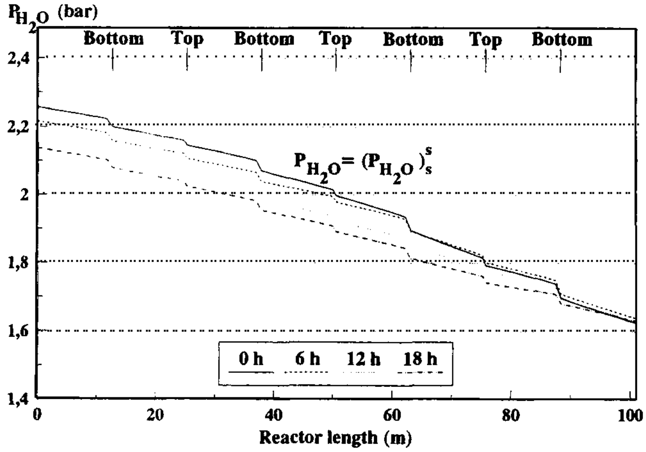

Figure 13. Evolution with time of the partial pressure profile of steam at the coke surface and in the process gas.

temperature that can be tolerated depends upon the tube material.

The combustion process can be further enhanced by increasing the air flow rate. The mass-transfer rate of oxygen to the coke surface increases, leading to a higher partial pressure of oxygen at the coke surface and also to an increase of the temperature peak at the upstream edge of the coke layer due to the exothermic combustion.

The evolution with time of the overall decoking rate profile is presented in Figure 14. Since the steam gasification rates were found to be much smaller than the combustion rates, the overall decoking rate is determined by the characteristics of the combustion rate profiles. At the early stages of the decoking operation, the rate profile exhibits a maximum as a function of the reactor length, due to the opposite effects on the intrinsic reaction rate of temperature and oxygen partial pressure at the coke surface. After 6 h of decoking, the decoking rate decreases continuously with the reactor length, because of the mass-transfer limitations.

Finally, the evolution with time of the mole fraction of oxygen and carbon dioxide at the coil outlet is shown in Figure 15. During the first 10 h of decoking, the amount of oxygen available for reaction is completely consumed. After 10 h of decoking, the mole fraction of oxygen at the coil outlet increases very rapidly with the decoking time. The measured evolution with time of the mole fraction of CO_2 at the coil exit coincides with the simulated values.

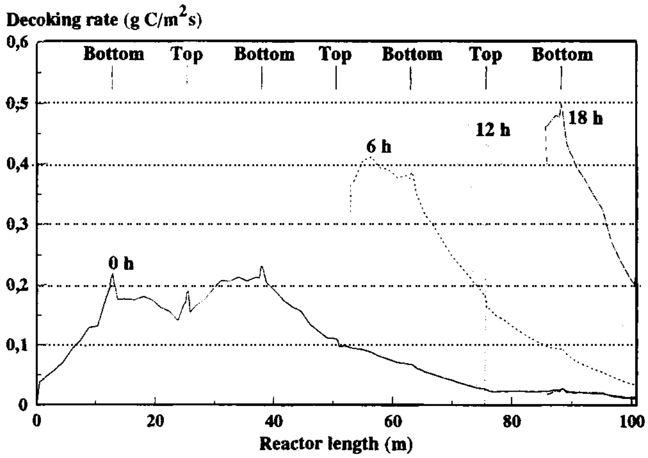

Figure 14. Evolution with time of the decoking rate profile.

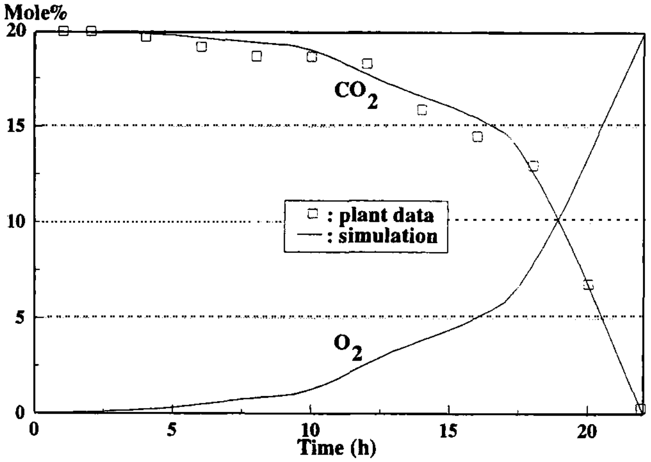

Figure 15. Evolution with time of the mole fraction of O_2 and CO_2 at the coil outlet.

Conclusion

The decoking operation in an industrial ethane cracking furnace with a single row of coils was simulated considering both the combustion and the steam gasification of the coke layer. A 1-D heterogeneous reactor model accounting for interfacial gradients was found to be necessary for the calculations. The initial profile of the coke layer thickness was obtained by a production run length simulation. The simulated conversion, product distribution, coil outlet temperature, maximum external tube skin temperature, total deposited amount of coke, and run length were compared with the actual plant values for the validation of the models. All were found to be in good agreement with the plant data.

The decoking simulation model provides a detailed understanding of the decoking operation and an accurate prediction of its duration. The gasification of the coke layer by steam was found to be reaction controlled and to occur in a broad zone of the reactor. The combustion process on the other hand was confined to a narrow zone, gradually moving through the reactor coil, as the coke layer is converted. The global combustion process was found to evolve from reaction to diffusion controlled conditions as a function of the decoking time.

The amount of unreacted oxygen at the coil outlet increases with the decoking time. The simulated tube skin and coil outlet temperatures, the exit O_2 and CO_2 contents, and the decoking run length were found to be in excellent agreement with the industrial observations.

The decoking simulation model can be applied in industrial operation for the optimization of the decoking. It can be used as a guide for the adaptation of the operating conditions (such as air and steam flow rate, and fuel gas flow rate), aiming at reducing the run length of the furnace while keeping the external tube skin temperature within limits. In the first place, the decoking can be accelerated by increasing the fuel gas flow rate per burner or adapting the firing pattern. This results in an increase of the external tube skin temperature, leading to an enhancement of the steam gasification. The combustion is not affected because of the diffusion limitations, but can be further enhanced by increasing the air flow rate.

Notation

A_i = surface of wall or tube zone i, m^2
a_v = surface of coke layer per volume unit reactor, m_r^2/m_r^3
c_p = heat capacity of the process gas, kJ/kg·K
c_{pc} = heat capacity of the coke layer, $kJ/kg_{cokes} \cdot K$
d_i = internal tube diameter, m
d_c = coke layer thickness, m
d_c^0 = initial coke layer thickness, m
d_r = reactor diameter ($= d_i - d_c$), m
G = total mass flux of process gas, $kg/m_r^2 \cdot s$
h_f = process gas convection coefficient, $kJ/m_r^2 \cdot s \cdot K$
$(k_g)_{O_2}$ = mass transfer coefficient of oxygen, $kmol/m_r^2 \cdot bar \cdot s$
$(k_g)_{H_2O}$ = mass transfer coefficient of steam, $kmol/m_r^2 \cdot bar \cdot s$
M_m = molecular weight of the process gas, kg/kmol
P_{O_2} = oxygen partial pressure in the process gas, bar
$P_{O_2}^0$ = oxygen partial pressure in the process gas at the coil inlet, bar
P_{H_2O} = steam partial pressure in the process gas, bar
$P_{H_2O}^0$ = steam partial pressure in the process gas at the coil inlet, bar
$(P_{O_2})_s^s$ = oxygen partial pressure at the coke surface, bar
$(P_{H_2O})_s^s$ = steam partial pressure at the coke surface, bar
P_t = total pressure, bar
P_t^0 = coil inlet pressure, bar
Q_i = heat flux for the tube zone i, kW/m^2
$Q(z)$ = heat flux used in the reactor coil simulation, kW/m^2
r_b = radius of tube bend, m
R_e = Reynolds number
r_{O_2} = reaction rate of oxygen, $kmol/m_r^2 \cdot s$
r_{H_2O} = reaction rate of steam, $kmol/m_r^2 \cdot s$
t = time, s
T = process gas temperature, K
T_0 = coil inlet temperature, K
T_i = temperature of zone i, K
T_r = temperature of surroundings, K
T_s^s = temperature at the coke surface, K
u = superficial flow rate, $m_g^3/m_r^3 \cdot s$
W_{zi} = black body emissive power of the zone i, kW/m^2
z = axial reactor coordinate, m
Z_iZ_j = total exchange area between zones i and j, m^2
Z_jZ_i = total exchange area between zones j and i, m^2

Greek letters

Λ = tube bend angle, °
$(-\Delta H)_{298.15}^0$ = standard heat of reaction at 298.15 K, kJ/mol
$(-\Delta H)_{O_2}$ = heat of the oxydation reaction (Eq. 1) (exothermic reaction: > 0), kJ/kmol
$(-\Delta H)_{H_2O}$ = heat of the gasification reaction (Eq. 2) (endothermic reaction: < 0), kJ/kmol
ρ_g = process gas density, kg/m_r^3
ρ_c = coke layer density, kg_{cokes}/m_{cokes}^3
σ = Stefan-Boltzmann constant, 5.7×10^{-8} $W/m^2 \cdot K^4$

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