A three-dimensional mathematical model has been developed for the simulation of flow, temperature and concentration fields in the radiation section of industrial scale steam cracking units. The model takes into account turbulence–chemistry interactions through the Eddy Dissipation Concept (EDC) model and makes use of Detailed Reaction Kinetics (DRK), which allows the detailed investigation of the flame structure. Furthermore, simulation results obtained with the EDC-DRK model are compared with simulation results obtained with a simplified model combining the Eddy Break Up (EBU)/finite rate formulation with Simplified Reaction Kinetics (SRK). When the EBU-SRK model is used, much faster fuel oxidation and products formation is predicted. The location of the peak temperature is shifted towards the burner, resulting in a smaller flame and the confinement of the combustion process into a smaller area. This is most likely because of the inherent deficiency of the simplified model to correctly predict the overall (effective) burning rate when the turbulent mixing rate and the reaction rate are comparable. It is shown that when neither the “fast-chemistry” nor the “slow-chemistry” approximation is satisfied, the overall burning rate is overpredicted. The smaller flame volumes obtained with the EBU-SRK model have important effects on the predicted temperature distribution in the furnace as well as on other significant design parameters like the refractory wall and tube skin temperatures. It is suggested that more sophisticated turbulence–chemistry interaction models like the EDC model and more Detailed Reaction Kinetics should be used for combustion modeling in steam cracking furnaces under normal firing conditions.

1. Introduction

Steam cracking of hydrocarbons is a basic petrochemical process since it accounts for the major part of the production of ethylene and propylene, which are the main building blocks for the petrochemical industry. Typical steam cracking furnaces are approximately 12 m long, 3 m wide and 8 m high. Steam cracking takes place in coils suspended in the radiation section of the furnace. The process gas that flows through the coils is heated up to high temperatures by means of gas-fired long flame burners distributed in the floor of the furnace and/or by means of gas-fired radiation burners in the side walls of the furnace.

An accurate simulation of the olefin yields, coke formation and NOx emissions requires accurate simulations of the flue gas and process gas flow patterns, of the process, tube, wall and flue gas temperature profiles as well as the heat fluxes that are exchanged between the process gas and the flue gas. Thus, simulation of all the interacting chemical and physical phenomena that take place in the radiation box and the process tubes are necessary.

At the Laboratory for Petrochemical Engineering (LPT) in-house developed software packages allow for coupled “fire-side” and “process-side” simulations of industrial scale steam cracking furnaces. For the simulation of the cracking reactions inside the reactor tubes a detailed kinetic radical reaction scheme (CRACKSIM) containing over 1000 reactions between 128 components has been developed (Willems & Froment, 1988a, 1988b). Coke formation models were derived for both light and heavy hydrocarbon feedstocks (Plehiers & Froment, 1990; Reyniers, Froment, Kopinke, & Zimmermann, 1994). The radical reaction scheme can be combined with a one-dimensional or a two-dimensional reactor model (COILSIM...
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>constant in the EBU model</td>
</tr>
<tr>
<td>( a )</td>
<td>stoichiometric reaction coefficient</td>
</tr>
<tr>
<td>( b )</td>
<td>stoichiometric reaction coefficient</td>
</tr>
<tr>
<td>( C )</td>
<td>concentration (mol/cm(^2))</td>
</tr>
<tr>
<td>( C_{1e} )</td>
<td>RNG ( k-\varepsilon ) model variable coefficient</td>
</tr>
<tr>
<td>( C_{k} )</td>
<td>RNG ( \varepsilon ) model constant</td>
</tr>
<tr>
<td>( C_{ns} )</td>
<td>variables in the six-flux radiation model</td>
</tr>
<tr>
<td>( D )</td>
<td>molecular diffusivity (m(^2)/s)</td>
</tr>
<tr>
<td>( D_{h} )</td>
<td>turbulent diffusivity (m(^2)/s)</td>
</tr>
<tr>
<td>( Da )</td>
<td>Damköhler number</td>
</tr>
<tr>
<td>( h )</td>
<td>characteristic flow time scale</td>
</tr>
<tr>
<td>( E )</td>
<td>total energy per unit mass, ( E = h + \frac{1}{2} u_{ij} + k ) (J/kg)</td>
</tr>
<tr>
<td>( g )</td>
<td>gravitational constant, ( g = 9.81 ) (m/s(^2))</td>
</tr>
<tr>
<td>( H_{eff} )</td>
<td>effective enthalpy per unit mass (J/kg)</td>
</tr>
<tr>
<td>( h_{m} )</td>
<td>mean static enthalpy per unit mass (J/kg)</td>
</tr>
<tr>
<td>( h_{m}^{*} )</td>
<td>static enthalpy of species ( m ) in the fine structures (J/kg)</td>
</tr>
<tr>
<td>( h_{m}^{n} )</td>
<td>turbulent kinetic energy per unit mass (m(^2)/s(^2))</td>
</tr>
<tr>
<td>( k_{0} )</td>
<td>absorption coefficient (m(^{-1}))</td>
</tr>
<tr>
<td>( K_{0} )</td>
<td>Kolmogorov number</td>
</tr>
<tr>
<td>( K_{t} )</td>
<td>Kolmogorov time scale</td>
</tr>
<tr>
<td>( L_{e} )</td>
<td>Lewis number of species</td>
</tr>
<tr>
<td>( m )</td>
<td>molar mass (kg/mol)</td>
</tr>
<tr>
<td>( M )</td>
<td>mass diffusivity of species ( m ) (m(^2)/s)</td>
</tr>
<tr>
<td>( N_{S} )</td>
<td>total number of species</td>
</tr>
<tr>
<td>( P_{k} )</td>
<td>production of turbulent kinetic energy term (J/m(^3)/s)</td>
</tr>
<tr>
<td>( P_{d} )</td>
<td>turbulent Prandtl number</td>
</tr>
<tr>
<td>( P_{eff} )</td>
<td>effective pressure, ( P_{eff} = P + \frac{1}{2} \rho u^{2} ) (Pa)</td>
</tr>
<tr>
<td>( Q_{rad} )</td>
<td>net volumetric rate of radiative heat release (J/m(^3)/s)</td>
</tr>
<tr>
<td>( q_{rad} )</td>
<td>net radiative heat transfer rate from the fine structures to the bulk fluid per unit mass of fine structures (J/kg/s)</td>
</tr>
<tr>
<td>( R )</td>
<td>ideal gas constant, ( R = 8.314 ) (J/mol/K)</td>
</tr>
<tr>
<td>( R_{m} )</td>
<td>average production rate of species ( m ) (mol/m(^3)/s)</td>
</tr>
<tr>
<td>( r_{k} )</td>
<td>total rate of reaction ( k ) (mol/m(^3)/s)</td>
</tr>
<tr>
<td>( r_{mix} )</td>
<td>turbulent mixing rate of reaction ( k ) (mol/m(^3)/s)</td>
</tr>
<tr>
<td>( r_{int} )</td>
<td>intrinsic rate of reaction ( k ) (mol/m(^3)/s)</td>
</tr>
</tbody>
</table>

Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>wall absorptivity</td>
</tr>
<tr>
<td>( \alpha_{e} )</td>
<td>RNG ( k-\varepsilon ) model constant</td>
</tr>
<tr>
<td>( \alpha_{k} )</td>
<td>RNG ( \varepsilon ) model constant</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>mass fraction of the fine structures</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>dissipation rate of turbulent kinetic energy per unit mass (m(^3)/s(^2))</td>
</tr>
<tr>
<td>( \varepsilon_{w} )</td>
<td>wall emissivity</td>
</tr>
<tr>
<td>( \eta )</td>
<td>turbulence to mean shear time scale ratio</td>
</tr>
<tr>
<td>( \eta_{0} )</td>
<td>RNG ( k-\varepsilon ) model constant</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>molecular conductivity (J/m/s/K)</td>
</tr>
<tr>
<td>( \lambda_{s} )</td>
<td>turbulent conductivity (J/m/s/K)</td>
</tr>
<tr>
<td>( \mu )</td>
<td>molecular viscosity (Pa/s)</td>
</tr>
<tr>
<td>( \mu_{t} )</td>
<td>turbulent viscosity (Pa/s)</td>
</tr>
<tr>
<td>( n )</td>
<td>kinematic viscosity (m(^2)/s)</td>
</tr>
<tr>
<td>( \rho )</td>
<td>mean density (kg/m(^3))</td>
</tr>
<tr>
<td>( \rho^{*} )</td>
<td>density in the fine structures (kg/m(^3))</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Stefan-Boltzmann constant, ( \sigma = 5.7 \times 10^{-8} ) (J/m(^2)/K(^4))</td>
</tr>
<tr>
<td>( \tau )</td>
<td>characteristic time scale of the fine structures (s)</td>
</tr>
<tr>
<td>( \tau_{m}^{*} )</td>
<td>characteristic time scale of the laminar flame (s)</td>
</tr>
</tbody>
</table>

1D/2D solving the flow and species transport equations in the reactor (Van Geem, Heynderickx, & Marin, 2004). The calculation of the accurate flow and temperature fields in the radiation box is done with CFD simulation software (FLOWSIM) that solves the three-dimensional Reynolds Averaged Navier-Stokes (RANS) equations along with a two-equation turbulence model. Since radiation accounts for most of the heat flux towards the reactor tubes there is also a strong need for an appropriate radiation model. Finally, for a furnace with long flame burners, where combustion occurs in the furnace itself, as opposed to furnaces with radiation burners, where combustion is localized in the burner cups, the CFD flow solver should also be combined with a combustion model including combustion kinetics and turbulent mixing. Examples of coupled “fire-side” and “process-side” simulations are given in Heynderickx, Oprea,
Marin, and Dick (2001), Oprins and Heynderickx (2003) and Oprins, Heynderickx, and Marin (2001). The focus in this work is on turbulent combustion modeling in steam cracking furnaces. In the aforementioned papers, combustion was modeled using Simplified Reaction Kinetics (SRK) accounting for hydrocarbon and hydrogen oxidation (Westbrook & Dryer, 1981) in combination with the Eddy Break Up (EBU)/finite rate formulation (Magnussen & Hjertager, 1976). In this work, the combustion model is extended to make use of Detailed Reaction Kinetics (DRK) in combination with a turbulent-chemistry interaction model based on the Eddy Dissipation Concept (EDC) (Gran & Magnussen, 1996). A representative segment of a steam cracking furnace is simulated both with the simplified and the more advanced turbulent combustion model. This work investigates the effect of the inclusion of detailed combustion chemistry and of an advanced turbulence-chemistry interaction model in CFD simulations of steam cracking furnaces on the predicted wall, tube skin and flue gas temperature profiles as well as on the predicted species concentration profiles. Moreover, the detailed combustion mechanism is used to obtain an insight into the structure of the furnace flames under normal furnace firing conditions.

2. Turbulent combustion in CFD simulations

Turbulent combusting flows are characterized by continuous fluctuations in density, temperature and species concentrations. Given the strong non-linear nature of the reaction rate expressions with respect to the state variables, closure of the system of reaction rate equations is not straightforward. Species reaction rates based on mean values of temperature and species concentration fluctuations with respect to the state variables, closure of the average reaction rate expression leads to fast and robust calculations. It is a first-order closure model and, like the flamelet models, was developed under the assumption of \( Da \gg 1 \) and \( Ko < 1 \).

Those approaches can be classified in three categories. In a first, statistical approach, the mean scalar values are extracted through the knowledge of one-point Probability Density Function (PDF)’s. The shape of one joint scalar or joint velocity scalar PDF can be determined by its own transport equation (e.g. Fox, 1996; Pope, 1985). This approach has the advantage that it treats the chemical source term exactly. It is not entirely model free though. The terms representing the transport of PDF in the velocity space due to velocity and pressure fluctuations and the transport of PDF in the reactive scalar space due to molecular diffusion appear unclosed in the PDF transport equation. Thus, the closure problem is shifted from the chemical source term to molecular mixing and mixing due to velocity and pressure fluctuations. The predictive capability of transport PDF methods heavily depends on the quality of modeling of the unclosed terms (Peters, 2000). The transport PDF equation is characterized by high dimensionality that renders classical techniques like the finite volume method inappropriate for its solution. Monte Carlo techniques are to be used. Although the method is theoretically sound, its application to industrial CFD problems with realistic chemistry is expected to be computationally very expensive even if multi-processor computers and advanced tabulation techniques are used.

Much simplification is obtained when the shape of PDF is pre-assumed (e.g. Jones & Whitelaw, 1982). Usually, either a \( \beta \)-function or the Gaussian function is used for that purpose. In this case, the first two moments (mean and variance) of a scalar suffice to determine its PDF. Under the simplification of equilibrium chemistry and \( Le = 1 \) for all species local species mass fractions and density are given as function of a so-called mixture fraction, which is a conserved quantity. Therefore, only two transport equations for the mean and the variance of the mixture fraction need to be constructed and solved. This is a popular approach leading to fast calculations but is only applicable to non-premixed combustion systems and gives only reliable results if the equilibrium assumption is satisfied.

A second class of turbulence-chemistry interaction methods is based on a geometrical analysis of the flame. Those models are related to the flamelet assumption (e.g. Bray & Peters, 1994). All reactions are considered to be sufficiently fast so that the length scale of the reaction zone is smaller than the Kolmogorov length scale. In this case, the flame can be considered as an ensemble of very thin, isotropic, one-dimensional laminar flame structures (‘flamelets’). The implementation of a flamelet model is not unique and depends on the type of the flame. Usually, the steady state governing equation for scalars in the flamelets is solved prior to the actual flame calculation resulting in the construction of flamelet libraries where values for the independent variables are stored for a wide range of a passive scalar such as the mixture fraction, which is a conserved quantity. Therefore, only one transport equation for a so-called mixture fraction, which is a conserved quantity is needed. Those libraries are later used during the CFD calculations to determine the local species distribution. Models belonging to this category are valid for \( Da \gg 1 \) and \( Ko < 1 \).

The third category of turbulence-chemistry interaction models consists of models that relate the effective reaction rates to turbulent mixing levels. Probably the most widely celebrated model of this category is the modified EBU model of Magnussen and Hjertager (1976). Its popularity stems from the fact that it leads to fast and robust calculations. It is a first-order closure model and, like the flamelet models, was developed under the assumption of \( Da \gg 1 \). A recent extension of this model is the EDC model (Gran & Magnussen, 1996) that was developed in order to be able to take into account detailed, finite rate chemistry. The latter model has the advantage of being applicable to both premixed and non-premixed combustion systems and has been successfully used in the past. Gran and Magnussen (1996) used the model for simulating a non-premixed bluff body stabilized flame. Good agreement with experimental data was reported. The performance of the EDC model was comparable with the one of a transport PDF model. Chakraborty, Paul, and Mukunda (2000) used the model to simulate H/air combustion in a scramjet combustor. In Han, Wei, Schnell, and Hein (2003), the EDC is used for simulation of a hybrid reburn/selective non-catalytic reduction process in a pilot scale coal-fired furnace in combination with a reduced kinetic model. In Giacomazzi, Battaglia, and Bruno (2004), the EDC model is used to describe single-step combustion chemistry close to the dissipation scales
in the context of Large Eddy Simulations (LES) and RANS simulations of a premixed C3H8/air bluff-body flame. Rasmussen et al. (2004) use the EDC model for post-processing of a detailed kinetic mechanism onto converged flow and temperature profiles derived from a CFD simulation with single-step chemistry. In the present work, the EDC model with detailed combustion chemistry is used in coupled flow-reaction simulations to model combustion in a steam cracking furnace. The same simulations are performed with the simplified EBU-SRK model that was used in the past. The differences in the results coming out of the two modeling approaches are interpreted in terms of the theoretical background associated with them in order to examine the validity of the simplifications involved in the second approach.

An overview of the model equations, the implementation of combustion chemistry in the in-house developed code FLOWSIM and the numerical solution procedures are given in the following sections.

3. Flow modeling

The calculation of the three-dimensional statistically stationary turbulent flow field in the furnace is based on the solution of the RANS equations in compressible formulation, closed with the $k$–$\epsilon$ model derived from the Renormalization Group method (RNG) (Yakhout, Orszag, Thangam, Gatski, & Speziale, 1992). The equations of the RNG $k$–$\epsilon$ model are of the same form as those of the standard $k$–$\epsilon$ model. The transport equations for mass, momentum, energy, turbulent kinetic energy and dissipation rate of turbulent kinetic energy are:

$$\frac{\partial}{\partial x_j} \left( \rho \frac{\partial u_j}{\partial x_j} \right) = 0 \quad (1)$$

$$\frac{\partial}{\partial x_j} \left( \rho \frac{\partial u_i}{\partial x_j} \right) = - \frac{\partial}{\partial x_j} \left( \frac{\partial P_i}{\partial x_j} \right) + \frac{\partial}{\partial x_j} \left[ \left( \alpha_i + \lambda \right) \frac{\partial T}{\partial x_j} \right] - \frac{\partial}{\partial x_j} \left( \sum_{n=1}^{NS} \alpha_i D_i \frac{\partial y_n}{\partial x_j} \right) + S_E \quad (3)$$

$$\frac{\partial}{\partial x_j} \left( \rho \frac{\partial u_k}{\partial x_j} \right) = \frac{\partial}{\partial x_j} \left( \alpha_k \frac{\partial u_k}{\partial x_j} \right) + P_i - \rho \frac{\partial}{\partial x_j} \left( \frac{\partial u_k}{\partial x_j} \right) \quad (4)$$

$$\frac{\partial}{\partial x_j} \left( \rho \frac{\partial u_j}{\partial x_j} \right) = \frac{\partial}{\partial x_j} \left( \frac{\partial \alpha_k}{\partial x_j} \right) + C_{i} \frac{\partial P_i}{\partial x_j} - C_{\alpha \alpha} \frac{\partial \rho}{\partial x_j} \quad (5)$$

where $P_i = 2 \mu_i S_{ij}; \mu_i = C_{\mu i} \rho \sqrt{\epsilon}; \lambda = \mu_i \rho / P_{eqc}; P_{eqc} = 0.9; C_{\mu i} = 0.8445; a_i = a_{eqc} = 1.39; C_{\alpha i} = 1.68$ and $C_{\alpha i} = 1.42 - \frac{2 \mu_i \rho S_{ij}}{S_{ij}^2}; \eta = \frac{\alpha_i}{2} \left( \frac{\partial u_i}{\partial x_j} \right); \eta_j = \frac{\partial u_j}{\partial x_i}; S = \sqrt{\sum_{ij} S_{ij}^2}; S_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right); n_0 = 4.38; \beta = 0.012; \rho = \rho (\epsilon + \rho B)$. The source term in the energy equation is the net volumetric heat release due to radiation ($Q_{rad}$).

4. Radiation modeling

The six-flux model of De Marco and Lockwood (1975) is used to calculate the radiative heat transfer in the furnace. As pointed out by Keramida, Liais, Fourti, Boudouvis, and Markatos (2000), the six-flux model can be applied to industrial gas furnaces with relative ease; it is numerically robust and yields accurate predictions. The model divides the total solid angle into six solid angles of magnitude $2\pi$ in which the radiation intensity varies. Each one of the solid angles is centered about one of the co-ordinate directions. In this case, only three of the resulting six equations are independent. Another three equations are found by integrating the radiative transfer equation in each of three pairs of infinitesimal solid angles in the co-ordinate directions. The second-order Ordinary Differential Equations (ODEs) describing the six-flux model under the assumptions of (1) grey medium, (2) absence of scattering and (3) index of refraction equal to unity, are:

$$\frac{\partial}{\partial x_i} \left( \frac{1}{k_{\alpha \beta}} \right) = - \frac{k_{\alpha \beta} (C_{\alpha} - C_{\beta})}{k_{\alpha \beta} T^4} \quad (6)$$

$$\frac{\partial}{\partial x_i} \left( \frac{1}{k_{\alpha \beta}} \right) = k_{\alpha} (C_{\alpha} - C_{\beta}) - k_{\alpha} T^4 \quad (7)$$

$$\frac{\partial}{\partial x_i} \left( \frac{1}{k_{\alpha \beta}} \right) = k_{\beta} (C_{\alpha} - C_{\beta} + 3C_{\alpha}) - k_{\alpha} T^4 \quad (8)$$

The boundary conditions of the model considering conservation of radiation energy at the furnace walls and coils are:

$$a_n C_{\alpha} = 2 \frac{\partial C_{\alpha}}{\partial x_i} (2 - a_n) = \epsilon_n \sigma T_n^4 \quad (9)$$

$$a_n C_{\alpha} = 2 \frac{\partial C_{\alpha}}{\partial x_i} (2 - a_n) = \epsilon_n \sigma T_n^4 \quad (10)$$

$$a_n C_{\alpha} = 2 \frac{\partial C_{\alpha}}{\partial x_i} (2 - a_n) = \epsilon_n \sigma T_n^4 \quad (11)$$

where the $n$ and $s$ are associated with the positive and negative co-ordinate directions. Finally, the local volumetric heat release due to radiation is expressed as a function of the coefficients $C_{\alpha}$:

$$Q_{rad} = \frac{a_n C_{\alpha} (C_{\alpha} + C_{\beta}) - 4k_{\alpha} \sigma T_n^4}{4} \quad (12)$$

The absorption coefficient $k_{\alpha}$ is calculated in each control volume by means of the exponential band absorption model of Edwards, Glasoe, Hauser, and Tuchischer (1967).

5. Combustion modeling

For steam cracking furnaces with long-flame burners, the species concentration fields are calculated by solving the species transport equations in averaged formulation:

$$\frac{\partial}{\partial x_i} \left( \rho \frac{\partial y_i}{\partial x_i} \right) = \frac{\partial}{\partial x_i} \left( \rho D_i \frac{\partial y_i}{\partial x_i} \right) + R_i \Phi_i \quad (13)$$

where $D_i = D_i (1 / \mu)$. 

Two models have been used to calculate the average net species production rates $\dot{r}_k$ for the combustion of a methane-hydrogen fuel mixture.

### 5.1. EBU-SRK model

In this model, the methane and hydrogen oxidation process is represented by a simplified reaction scheme:

$$\text{CH}_4 + 1.5 \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2 \text{O}$$ (14)

$$\text{CO} + 0.5 \text{O}_2 \rightarrow \text{CO}_2$$ (15)

$$\text{H}_2 + 0.5 \text{O}_2 \rightarrow \text{H}_2 \text{O}$$ (16)

with corresponding intrinsic reaction rate equations:

$$r_{14,\text{intr}} = 1.5 \times 10^{13} e^{125604/RT} C_{\text{CH}_4} C_{\text{O}_2}^{-1.3}$$ (17)

$$r_{15,\text{intr}} = 3.98 \times 10^{20} e^{-167412/RT} C_{\text{CO}} C_{\text{O}_2}^{0.5} C_{\text{H}_2}^{0.25}$$ (18)

$$r_{16,\text{intr}} = 10^{13} C_{\text{O}_2}^{0.5} C_{\text{H}_2}$$ (19)

The intrinsic reaction rates for the two-step mechanism describing methane combustion (Eqs. (17) and (18)) were derived by Westbrook and Dryer (1981). The set of kinetic parameters in Eq. (19) was found to give reaction rates close to those of Westbrook and Dryer (1981). The set of kinetic parameters is represented by chemical kinetics. In other words, the system proceeds away from chemical equilibrium. A more extensive discussion on the EBU model and its limitations can be found in Brink, Mueller, Kilpinen, and Hupa (2000).

### 5.2. EDC-DRK model

In this model, the detailed combustion mechanism of Chen and Dibble (1991) is used. This mechanism involves 35 elementary reactions among 16 species: CH$_4$, H$_2$O, CO$_2$, H$_2$, CO, N$_2$, O, H, OH, HO$_2$, H$_2$O$_2$, CH$_3$, CH$_2$O, CH,O and HCO.

The EDC model is used to introduce turbulence-chemistry interactions. The model is based on a general reactor concept for the calculation of the average net species production rates in turbulent reactive flows. Combustion takes place in the regions of the turbulent field where the highest molecular fluxes occur. Those regions are associated with the smallest turbulence structures, the so-called fine-structures. Through a step-wise description of the turbulence energy cascade process from large to progressively smaller eddies, an expression for the mass fraction $\gamma^*$ of the fine-structures and for the characteristic time scale $\tau^*$ for mass exchange between the fine-structures and the bulk fluid is derived, dependent upon the turbulence quantities and the viscosity:

$$\gamma^* = 9.6 \left( \frac{L_\infty}{v} \right)^{1/4}$$ (21)

$$\tau^* = 0.41 \left( \frac{L_\infty}{v} \right)^{1/2}$$ (22)

These quantities are subsequently used in the reactor modeling of the fine structures. It is concluded that the model provides a link between the small-scale turbulence structures (or fine-structures), where reactions take place, and the grid-scale turbulence structures that can be described by turbulence models like the RNG $k-\varepsilon$, which is used in this work. A detailed analysis of the turbulence energy cascade model that was used to derive the expressions Eqs. (21) and (22) can be found in Ertesvåg and Magnussen (2000).

When the EDC model is to be integrated in a CFD code like FLOWSIM every single computational cell is considered to be composed of a reactive space, namely the fine-structures and the surrounding fluid that is inert. The reactive space is modeled as a Perfectly Stirred Reactor (PSR) exchanging mass and energy with the surrounding inert fluid. Thus, the solution of a PSR problem in every single cell involving the system of non-linear algebraic equations consisting of the mass and energy balances is required. To make the simulations more robust, temporal derivatives are added in the balances and the set of non-linear algebraic equations is transformed into an initial value problem where the ODE set of mass and energy balances (Eqs. (23) and (24)) is integrated from a known initial state to steady-state.

$$\frac{d\gamma^*_m}{dt} = \frac{\gamma_m - \gamma^*_m}{(1 - \gamma^*)^{m+1}} - \frac{a_\infty M_m}{\rho^m} \text{ (m = 1, ..., NS)}$$ (23)

$$\frac{d\theta^*_m}{dt} = \frac{\theta_m - \theta^*_m}{(1 - \gamma^*)^{m+1}} + \frac{\theta^*_m}{\rho^m}$$ (24)

The superscript asterisk refers to quantities in the fine structures. If there is no superscript (ref. Eq. (13)) averaged quantities over the cell are meant. In Eq. (24) the net radiative heat transfer rate $\dot{q}_{rad}$ from the fine-structures to the surrounding fluid is neglected.
In this work, the implicit Euler method is used for time marching when solving the set of ODE's. As only the steady-state solution is needed, relatively large time steps can be taken, thus reducing the required number of iterations and the required CPU time.

Solution of the system of Eqs. (23) and (24) provides values for the variables in the fine structures \( T^*, \delta T^* \) and for the net species production rates \( \dot{m}^* \) in the fine-structures. Eventually, the average net species production rates, \( R_m \), that are substituted in the species transport equations (Eq. (13)), which are integrated over each control volume, are calculated from:

\[
R_m = \frac{\gamma^*}{\left(1 - \gamma^*\right)^2} \left( \rho m^* - \rho m \right) \tag{25}
\]

Thus, the effect of turbulence on the source terms, \( R_m \), of the species transport equations (Eq. (13)) is taken into account through the determination of the mass fraction and of the characteristic time scale of the fine structures.

In principle, the EDC model can be combined with one- or two-step global mechanisms. However, the combination of the EDC model with the specific two-step mechanism for methane oxidation described in Section 5.1 was found to be problematic due to the negative concentration exponent for methane in Eq. (17), which satisfies the experimentally observed rich flammability limit of the methane/air mixture. From a numerical point of view, the negative exponent can create problems since the rate of methane consumption increases without limit as the methane concentration goes to zero. For that reason the PSR simulations failed to converge when the reaction rate Eq. (17) was used. Artificial truncation of the rate expression at a predetermined value did not solve the problem either. On this score, there are no simulation results with the EDC model and the global mechanism of Section 5.1. To our knowledge, no other set of values for the methane and oxygen concentration exponents have been proposed in the literature for use into technical kinetic expressions. Remark that when reaction rate Eq. (17) is combined with the EBU model this problem does not arise because at small fuel concentrations the mixing rate becomes smaller than the reaction rate and the total rate is set equal to the mixing rate.

Finally, it was shown by Gran and Magnussen (1996) that the EBU model (Eq. (20)) is a limiting case of the EDC model in the event of one-step irreversible reaction under the “mixed is burnt” (“fast-chemistry”) assumption.

5.3. Analysis of possibilities and limitations of the EBU model

This paragraph is focused on the investigation of the assumptions hidden in the mathematical formulations of the EBU and the finite rate chemistry/EBU models. The target is to bring out the inaccuracies that should be expected in the event that these models are used when mixing and reaction time scales are comparable. This discussion is also important for the interpretation of the results that are presented in Section 8. The EBU model is a “fast-chemistry” model and assumes that the effective reaction rate is only determined by the turbulent mixing rate as long as mixing and not reaction is the rate-limiting step. Combustion is seen by the model as a sequential process. First, the eddy break up process leads to enhanced molecular mixing at the small turbulence scales, the so-called fine-structures, and then reaction occurs in the fine-structures. Then the overall rate should be given from:

\[
r_k,i \approx \frac{1}{\tau_{mix}^*} \left( \frac{\tau_{mix}^*}{\tau_{chem}^*} \right) \left( \frac{\rho m^*}{\rho m} \right) \tag{26}
\]

This equation, however, may cause numerical problems in the calculation of the overall rate and therefore it is not used in the literature. Moreover, the state of the fine structures cannot be calculated in the context of the EBU model. The model neglects the second term in Eq. (26), which always leads to overestimation of the overall rate if the “fast-chemistry” assumption \( \tau_{mix}^* \ll \tau_{chem}^* \) is invalid. This is likely to happen at low temperature combustion \( T < 1300 \text{K} \) in the beginning of the reaction zone. The model also provides a simple “fix” for the “slow-chemistry” limit whenever the reaction rate is smaller than the mixing rate. In this case, the overall rate is set to be the reaction rate, which is calculated based on the average values of the state variables over the control volume. This is valid only for perfectly mixed components in the control volume where the temperature and concentration fluctuations go to zero. Again, neglect of the turbulent fluctuations causes overprediction of the overall rate (Bakker, Haidari, & Marshall, 2001) unless the “perfect-mixing” assumption holds. Given the fact that the EBU model can only be combined with one- or two-step global combustion mechanisms, the fuel consumption rate and equivalently the products formation rate is bound to be overpredicted if neither the “fast-chemistry” nor the “slow-chemistry” assumption is satisfied.

6. Numerical methods—solution procedure

The flow, combustion and radiation models are embedded in three different modules that are successively used in an iterative cycle, till convergence is reached. Spatial discretization of the flow domain is done by means of the finite-volume method using a non-structured tetrahedral grid created by the Gmsh software (Geuzaine & Remacle, 2001). The convection operator in all transport equations is discretized by means of a first-order flux-difference splitting scheme (Dick, 1990; Dick & Stejlant, 1997). Second-order terms are discretized centrally. The linearized set of partial differential equations in the flow and combustion models are solved point-wise with the LAPACK routines (Anderson et al., 1999), which employ the LU decomposition and back substitution method, using a Gauss–Seidel relaxation scheme. The latter means that at any iteration level the most recent values for the variables are used, which in general increases the convergence rate. Applying this relaxation scheme to the solution of the system of Eqs. (1)–(5) involves first sweeping forward and then backward through the list of cells and solving the system for the vector of primitive variables \( (\rho, u, v, w, p, k, r) \). No special consideration was given to
reordering of the cells before the Gauss–Seidel method was applied. The cell list remained as ordered by the grid generation program.

7. Furnace geometry and operating conditions

The objective of this work is two-fold. First, to investigate whether turbulence–chemistry interactions and detailed chemistry effects in the flame modeling of steam cracking furnaces influence the evolution of important dependent variable profiles, such as tube, wall and flue gas temperatures and fuel/flue gas species concentrations. Second, to obtain a clear conception of the flame structure. For that reason, a representative segment of a naphtha cracking furnace is simulated using the two combustion models described in Sections 5.1 and 5.2. The segment contains two flame burners that are positioned on the left and the right side of six reactor tubes. Fuel and air are premixed before entering the radiation section. 53222 tetrahedral cells are used to discretize the physical space between the segment walls, the symmetry planes and the reactor tubes. Local grid refinement is applied in the flame region above the two burners and near the solid boundaries.

In this work, no coupled furnace-reactor simulations (e.g. Heynderickx et al., 2001; Oprins et al., 2001) are performed, since only a segment of the furnace is simulated. Therefore, a fixed process gas temperature profile, taken from previous reactor calculations, is applied and is considered to be part of the boundary conditions of the simulations.

A schematic representation of the furnace and the simulated segment is given in Fig. 1. The top view of this volume element is presented in Fig. 2. The basic simulation conditions are given in Table 1.

8. Results and discussion

Simulation results from the application of the mathematical models described in Sections 3–5 to CH₄/H₂ premixed flames in a representative segment of a steam cracking furnace under normal firing conditions are presented. The results are mainly given in terms of temperature and species concentration profiles.

In Fig. 3, the calculated temperature profiles with the two combustion models in a vertical cross section through the burners are presented. A more extended reaction zone is predicted with the EDC-DRK model. The latter implies slower combustion of the fuel leading to lower temperatures in a small region close to the burners and higher temperatures further away from the burner. In order to quantify those differences, vertical and horizontal temperature profiles in the same vertical cross section are shown in Figs. 4 and 5.

In Fig. 4, the vertical temperature profile along the centerline of the right-hand side burner is presented. It is shown that the temperature evolution with the EDC-DRK model lags the temperature evolution with the EBU-SRK model up to approx-
Table 1
Simulation conditions

Furnace segment
- Height (m): 6.796
- Length (m): 1.2
- Width (m): 3.0
- Thickness of refractory (m): 0.23
- Thickness of insulation (m): 0.05
- Number of burners: 2

Reactor
- Number of reactor tubes: 6
- Total reactor length (m): 38.68
- External tube diameter (m): 0.12
- Internal tube diameter (m): 0.10

Firing conditions (one burner)
- Fuel gas flow rate (kg/s): 0.4226
- Fuel equivalence ratio: 0.94
- Fuel gas composition (wt%)
  - CH₄: 94.3%
  - H₂: 5.7%

Material properties
- Emissivity of furnace wall: 0.85
- Emissivity of tube skin: 0.6
- Thermal conductivity of refractory wall (W/mK): 0.394
- Thermal conductivity of insulation (W/mK): 0.19
- Thermal conductivity of tube skin (W/mK): \(-8.42 \times 10^{-2} + 3.04 \times 10^{-2} T (K)\)

Fig. 3. Temperature profile in a vertical cross section through the burners. (a) EDC-DRK model and (b) EBU-SRK model. Simulation conditions are given in Table 1.

Fig. 4. Vertical temperature profile along the centerline of the right-hand side burner. Simulation conditions are given in Table 1.

imimately 1.7 m above the burner opening. At this height the two lines cross and further downstream the temperature predicted with the EDC-DRK model remains higher but the temperature difference between the two models decreases with height. The maximum temperature predicted with the EDC-DRK model is 1918 K at approximately 2 m height whereas the maximum temperature predicted with the EBU-SRK is 1878 K at approximately 1.4 m height. Temperature differences up to 900 K are predicted in the region between the burner opening and the crossing point of the two temperature lines.
In Fig. 5, horizontal temperature profiles in the same cross section are presented. At 0.6 m height (Fig. 5a) similar trends are observed as in Fig. 4. Namely, much higher temperatures are predicted with the EBU-SRK model in the region close to the burners. The two temperature lines cross at approximately 0.3 m to the left of the right-hand side burner and 0.3 m to the right of the left-hand side burner. In the region between the crossing points and the reactor tubes the temperatures predicted with the
EDC-DRK model are higher but the temperature differences are gradually alleviated as the center of the furnace is approached. In the center of the furnace, where the tubes are located, a clear local minimum in the flue gas temperature is observed, the so-called heat sink expanding over the total furnace height, due to the presence of the tubes. The temperature profiles at the height of 3.5, 5 and 6.5 m (Fig. 5b–d) are outside of the flame zone where only flue gas is present. As already mentioned, the temperatures predicted with the EDC-DRK model are always higher than the temperatures predicted with the EBU-SRK model. More important is to notice the increasing asymmetry of the temperature profile with the furnace height. That can be attributed to the flow pattern in the furnace, shown in Fig. 6. A large recirculation zone is predicted by both combustion models in the upper left part of the furnace and it is somewhat extended when the EBU-SRK model is used. The recirculation zone starts from the left wall at a height of 3.5 m approximately and expands to the upper wall of the furnace and towards the reactor tubes. This recirculation zone is due to the asymmetric outlet of the flue gas in the furnace. Due to the high residence time of the flue gas in the recirculation zone, the temperature in this region becomes uniform (see Fig. 3) and the temperature difference predicted with the two combustion models remains constant (see the nearly flat part of the lines on the left-hand side of the horizontal temperature profiles in Fig. 5c and d). On the contrary, the temperature differences outside of the recirculation zone predicted with the two models decrease when going from the centerline of the burners towards the tubes, but this effect becomes more pronounced higher up in the furnace. This is because the effect of the recirculation zone on the temperature levels at the center of the furnace, where the reactor tubes are located, becomes stronger at higher heights, i.e. close to the upper furnace wall. The flue gas temperature distribution in the reactor tube region is important because it is an important factor determining the heat flux distribution towards the tubes and the tube skin temperature profile, which is presented in Fig. 7 and discussed next.

In Fig. 7, the internal tube skin temperature profile along the reactor length in the furnace segment is presented. As expected based on the presented flue gas temperature profiles, higher internal tube skin temperatures are predicted with the EDC-DRK.
model all along the reactor length. The ascending temperature trend that is predicted is due to the increasing process gas temperature. Six local minima are calculated with both models, which correspond to the points where the reactor passes the top of the furnace and the flue gas temperatures are low. Six local maxima are calculated on each one of the six tubes, 1.5–2 m above the furnace floor. Those are also the peak temperature heights of the two flames. The highest internal tube skin temperature differences, up to 20 K, between the two combustion models are predicted at the top part of each tube where the flue gas temperatures differ most. This issue has already been discussed in the previous paragraph.

The effect of the different combustion models on the wall temperatures is presented in Fig. 8. In this figure, the temperature variation with height on the A wall (Fig. 2) at three different axial positions (y-direction, Fig. 1) are presented. Following the presented flue gas temperature profiles, the wall temperatures predicted with the EDC-DRK model are constantly higher in all three cases. The temperature differences are between 25 and 60 K. Higher A wall temperatures are predicted between 1 and 2 m height above the furnace floor because this zone faces the right-hand side flame directly. The maximum A wall temperature predicted with the EDC-DRK model is 1585 K at y = 0.6 m (cross section through the burners) and z = 1.15 m (on the opposite of the peak temperature zone of the flame). The A wall temperatures decrease with height and reach the lowest values just below the outlet. The form of the temperature profiles on the C wall is similar to that of the A wall and therefore they are not presented in this paper.

The temperature differences predicted with the two combustion models and presented in the previous paragraphs suggest different fuel combustion rates. The concentration profiles of the two fuel components, that is methane and hydrogen, in the same cross section where the temperature profiles have been presented are shown in Fig. 9. The results are presented in grey scaling and the black isolines named A–C correspond to different CH₄ and H₂ concentration levels. It is readily noticed that combustion progress for both fuel components is slower in the case of the EDC-DRK model, leading to larger flames when this model is used. Indicatively, it is mentioned that 75% of the amount of CH₄ at the inlet has been consumed at 0.85 m height (line B) with the EBU-SRK model whereas the same amount of methane is predicted to have been consumed at 1.2 m height with the more advanced EDC-DRK model. The differences are striking in the case of H₂. For example, 99% of H₂ has already been burnt at 0.9 m height (line C) with the EBU-SRK whereas the peak of the line C with the EDC-DRK is almost three times higher.

Similar results are obtained for the concentration profiles of the major combustion products, namely CO₂ and H₂O (Fig. 10).
The white isolines A–C indicate the progress of CO₂ and H₂O formation at three different levels, which are 50, 75 and 99%, respectively, of their maximum values. Slower formation of both products is predicted in the case of the EDC-DRK model. For instance, 99% of CO₂ has been formed at 2 m height (line C) with the EBU-SRK model and at 2.3 m height with the EDC-DRK model. Moreover, it can be seen that the differences in the H₂O evolution with the two combustion models are even more pronounced. The differences in the temperature and concentration profiles that have been presented so far with the two combustion models can be explained by means of the physics that are associated with them. This discussion has already been done in Section 5.3.

A second goal of this work was to obtain an insight into the flame structure. The detailed combustion mechanism is used to obtain an understanding of the detailed structure of the CH₄/H₂/air premixed flames in the furnace. Fig. 11 shows the most important species concentration profiles along the centerline of the right-hand side burner. In Fig. 11a, the concentration profiles of the main C-containing species CH₄, CO, CO₂ are presented. It is observed that the maximum CO concentration is approximately situated at the same height where the CH₄ concentration goes to zero. Moreover, the concentration profiles of CO, CO₂ and CH₄ as well as that of H₂O (Fig. 11b) become noticeably steeper above 1 m height approximately. It is also remarked that the CO curve is always below the CO₂ curve although the opposite would be expected in the beginning of the reaction zone since CO₂ is mainly formed by the oxidation of CO. To interpret the above results, Fig. 12 should be considered together with the flow field presented in Fig. 6. In Fig. 12, the average net species production rates of the fuel components and the main combustion products (Rₘ) along the centerline of the right-hand side burner are presented. It is important to notice that the bulk of chemical activity is between 1 and 2.5 m height, which explains why the fuel species and products concentration profiles (Fig. 11a and b) as well as the temperature rise (Fig. 4) become steeper above 1 m height. It can be seen in Fig. 4 that the temperature at 1 m height is 840 K approximately. The temperature rise from the inlet temperature of 343 up to 840 K where combustion starts, is due to conductive heat fluxes from the high temperature region back to the preheat zone and due to convective heat fluxes associated with the circulating hot flue gas from
Fig. 11. Vertical species mass fraction profiles along the centerline of the right-hand side burner. (a) $y_{CO_2}$, $y_{CH_4}$ and $y_{CO}$; (b) $y_{H_2O}$, $y_{CH_2O}$ and $y_{H_2O_2}$; (c) $y_{CH_2O}$, $y_{CH_3O}$ and $y_{CH_3}$; (d) $y_O$, $y_H$ and $y_{OH}$. Model: EDC-DRK. Simulation conditions are given in Table 1.

Fig. 12. Calculated vertical profiles of some selected average net species production rates along the centerline of the right-hand side burner. Model: EDC-DRK. Simulation conditions are given in Table 1.

The reaction zone (Fig. 6). Those large recirculation zones are also responsible for the presence of CO$_2$ in the preheat zone (up to 1 m height) in higher amounts than CO, whereas results from one-dimensional premixed flame calculations (without recirculation) show that CO$_2$ formation lags CO formation in the beginning of the reaction zone. In Fig. 12 it is seen that the maximum product formation rates (CO$_2$ and H$_2$O) are calculated exactly where the maximum destruction rates of the fuel species (CH$_4$ and H$_2$) occur. Above that height (approximately 1.3 m) the chemical activity declines and at 2.5 m it is completed. At this height, the CO$_2$ and H$_2$O concentrations have reached their maximum values (Fig. 11a and b). Besides, the peak of the CO$_2$ formation rate almost corresponds spatially with the peak of the CO concentration (Fig. 11a) because CO$_2$ is formed through the recombination reaction of CO with OH radicals. It is also noted that C-intermediate species such as CH$_3$, CH$_2$O and CH$_3$O (Fig. 11c) as well as H-intermediate species such as OH$_2$ and H$_2$O$_2$ (Fig. 11b) coexist in the same interval between 0 and 2.5 m. Moreover, their peak concentration values are found to be at the same height of approximately 1.2 m. Finally, the calculations with the detailed combustion mechanism have revealed that the OH mass fraction is roughly one order of magnitude higher than the mass fraction of O and two orders of magnitude higher than the mass fraction of H (Fig. 11d), which suggests that for the fuel and the firing conditions considered, OH is the dominant radical in the H$_2$–O$_2$ pool.
9. Conclusions

A three-dimensional mathematical model has been developed for the simulation of flow, temperature and concentration fields in the radiation section of industrial scale steam cracking units. The model takes into account turbulence-chemistry interactions through the Eddy Dissipation Concept model and makes use of Detailed Reaction Kinetics, which allows the detailed investigation of the flame structure. Furthermore, simulation results obtained with the EDC-DRK model are compared with simulation results obtained with a simplified model combining the Eddy Break Up linear finite rate formulation with Simplified Reaction Kinetics. When the EBU-SRK model is used, much faster fuel oxidation and products formation is predicted. The location of the peak temperature is shifted towards the burner, resulting in a smaller flame and the confinement of the combustion process into a smaller area. This is most likely because of the inherent deficiency of the simplified model to correctly predict the overall (effective) burning rate when the turbulent mixing rate and the reaction rate are comparable. It is shown that when neither the “fast-chemistry” nor the “slow-chemistry” approximation is satisfied the overall burning rate is overpredicted. The fact that smaller flame volumes are calculated with the EBU-SRK model has an important effect on the predicted temperature distribution in the furnace as well as on other significant parameters like the refractory wall and tube skin temperatures. It is therefore concluded that more sophisticated turbulence-chemistry interaction models like the EDC model and more Detailed Reaction Kinetics should be used for combustion modeling in steam cracking furnaces under normal firing conditions.

Acknowledgements

The authors wish to acknowledge the Fund for Scientific Research—Flanders (FWO-N) for financial support through project No. G.0070.03. Bart Merci is Postdoctoral Researcher of the FWO-N.

References


