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ULTRA RICH COMBUSTION OF NATURAL GAS TO SYNGAS

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ABSTRACT

In this paper the turbulent rich combustion process of perfectly premixed natural gas and oxidizer to syngas is investigated. Also an overview is given of an ultra rich combustion setup that is present at the Laboratory of Thermal Engineering of the University of Twente.

The numerical investigation of the process is carried out as follows. The gaseous chemistry is described by a reaction progress variable based combustion model with detailed chemistry. The soot formation is described by the processes of nucleation, surface growth, agglomeration and oxidation. Also radiative heat loss of the gases and the soot particles is taken into account. The numerical model predicts the flow field, gaseous species, temperature, heat loss and soot mass fraction and number of soot particles.

The combination of radiation and soot formation models with the combustion model will give a complete picture of the processes in the partial oxidation reactor.

The numerical results will be validated with measurements on a reactor operating at pressures from 1 to 6 bar and at equivalence ratios 2 to 4. The measurements are to be done by taking samples from the reactor which are subsequently analyzed with a gas chromatograph and a Scanning Mobility Particle Sizer.

The planned experiments will give valuable validation data for the performance of combustion and soot formation models at ultra rich conditions that are not yet available in literature.

INTRODUCTION

Ultra rich combustion (partial oxidation) of natural gas is a process applied to produce synthesis gas (or syngas). This gas is composed primarily of hydrogen and carbon monoxide. Syngas represents the intermediary step from hydrocarbons to bulk chemicals and synthetic fuels. The ultra rich combustion of natural gas is exothermic. Due to the high temperature and pressure of the syngas produced, the syngas sensible heat can be efficiently converted to power by expansion in a gas turbine. The power is used to run an air separation unit, which provides the necessary oxygen to the partial oxidation process. This way, the partial oxidation process has a high efficiency heat recovery system and is independent of external sources of energy.

The reactor design and the operating conditions have to ensure a high conversion of natural gas to hydrogen and carbon monoxide. In addition to this, the hydrogen to carbon monoxide ratio in the syngas is relevant for the downstream application of the syngas produced. The syngas soot content is also of concern, in view of the syngas fouling the reactor system and to minimize the downstream effort of soot removal.

The goal of the research is the development of a numerical model which can be used as a design tool for the partial oxidation reactor. The operating conditions for the large scale application of the partial oxidation process are characterized by turbulent flow and a high fuel to oxidizer ratio, far beyond the stoichiometric ratio.

MODELING

In this section the modeling of the rich combusting flow field is discussed. First the transport equations for a combusting flow field are given. Next the combustion model principles are discussed and its transport equations are shown. The last part consists of a discussion of the model that is going to be used to predict soot formation.

Transport equations for a combusting flow field

Following the assumptions below, the Favre averaged transport equations describing a combusting flow field (in index notation) are given in equations 1-4:

- Viscous force tensor described by Newton's Law.
- Molecular diffusive fluxed described by Fick's Law.
- Enthalpy diffusive flux described by Fourier's Law.
- Body forces neglected.
- Low Mach number assumption.

Mass:

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_j}{\partial x_j} = 0$$

Momentum (i=1,2,3):

$$\frac{\partial \bar{\rho} \tilde{u}_i}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_j \tilde{u}_i}{\partial x_j} - \mu_l \frac{\partial^2 \tilde{u}_i}{\partial x_j \partial x_j} + \frac{\partial \bar{\rho} \overline{u}_j \tilde{u}_i}{\partial x_j} + \frac{\partial \bar{p}}{\partial x_i} = 0$$
(2)

Species (k = 1,...,N):

$$\frac{\partial \bar{\rho} \tilde{Y}_{k}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_{j} \tilde{Y}_{k}}{\partial x_{j}} + \frac{\partial \bar{\rho} \overline{u_{j}' Y_{k}''}}{\partial x_{j}} = \frac{\partial}{\partial x_{j}} \left(\bar{\rho} D_{k} \frac{\partial \tilde{Y}_{k}}{\partial x_{j}} \right) + \overline{\omega_{k}}$$
(3)

Total enthalpy:

$$\frac{\partial \bar{\rho} \tilde{h}_t}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_j \tilde{h}_t}{\partial x_j} + \frac{\partial \bar{\rho} \overline{u_j'' h_t''}}{\partial x_j} = \frac{\partial}{\partial x_j} \left(\bar{\rho} D_k \frac{\partial \tilde{Y}_k}{\partial x_j} \right) + \overline{q^{rad}}$$
(4)

In the above set of equations unclosed terms appear. Turbulent combustion modeling must provide find closures for these terms.

The CFI model

The most accurate way of describing combustion with equations 1-4 is to solve the transport equation 4 for the total enthalpy and the transport equation 3 for each species. Transport equation 3 can be solved with the use of a reaction mechanism consisting of a collection of elementary reactions and temperature, pressure and species concentration dependent reaction rates. There are several reaction mechanisms for specific types of combustion. The more detailed mechanisms often consist of hundreds of species and reactions. A downside of a detailed mechanism is however that the number of species transport equations that have to be solved is high and thus computationally very expensive. Furthermore, the chemical system consists of fast and slow timescales which can vary up to several orders of magnitude. This makes the system stiff and thus difficult to solve. Therefore the number of species transport equations has to be reduced.

The CFI combustion model, developed at the Laboratory of Thermal Engineering of the University of Twente, is capable of modeling the mixing of fuel, detailed chemistry and heat loss in turbulent combustors accurately with a limited number of transport equations. The backbone of the CFI model consists of three dimensionless scalars: c, f and i. The reaction progress variable c is a measure to what extent a mixture of gases is in equilibrium. The CFI model allows the existence of a general number of reaction progress variables, so that c becomes a Sx1 vector with S reaction progress variables. Mixing and heat loss are taken into account through the use of respectively a mixture fraction scalar f and an enthalpy scalar i.

The CFI model uses a reduced mechanism in order to reduce the stiffness and the number of species transport equations. Creating a reduced mechanism can be manually as well as automatically. Manual reduction of larger mechanism is very complex, therefore in the CFI model a more general approach is applied. The CFI model uses the Computational Singular Perturbation (CSP) method [1] to automatically generate the reduced mechanism.

The CSP method

(1)

A chemical reaction can be regarded as a path through a multi-dimensional composition space in which each dimension is a concentration of a chemical species. The composition of a chemical system can be represented as a point in this space. Chemical-kinetic rate equations of the system determine the path of the composition point towards an equilibrium point. Fast time scales, generated by fast reactions, move the point to a part of the complete domain that is dictated by the slow time scales, the so called low-dimensional manifold. The point then moves along this low-dimensional manifold towards an equilibrium point. If perturbations move the point outside the low-dimensional manifold, the fast reactions take care of a rapid return. The CSP algorithm is capable of specifying the low-dimensional manifold. First, the steady state species are distinguished from the non-steady. Steady state species are the species associated with the fastest chemical timescales. Second, the fast reactions corresponding to the steady state species are removed from the reaction mechanism, so that only the low-dimensional manifold remains. The removal of the fast timescales has as result that the reduced mechanism becomes less stiff. The manifold is then parameterized by a set of linear independent variables.

Definition *c*, *f* and *i*

The mixture fraction scalar *f* is defined as:

$$f = \frac{Y_E - Y_E^{in2}}{Y_E^{in1} - Y_E^{in2}}$$
(5)

 Y_E is the element mass fraction of an element *E*, *in1* and *in2* indicate the element mass fraction on inlet 1 and inlet 2. If it is assumed that the diffusivities are equal, the mixing problem is greatly simplified. The mixture fraction *f* is then independent of the choice of the element *E* in equation 5 [12]. A property of element mass fractions is that they can only be changed by mixing. Therefore also *f* is created nor destroyed in chemical reactions and thus a conserved scalar. The mixture fraction moves between 0 (composition inlet 2) and 1 (composition inlet 1).

The reaction progress variable *c* is defined as:

$$c = \frac{\hat{Y} - \hat{Y}^{ub}}{\hat{Y}^{eq} - \hat{Y}^{ub}} = \frac{\hat{Y} - \hat{Y}^{ub}}{W}$$
(6)

In this definition \hat{Y} is a composed species based on the species mass fractions (i = 1,...,N):

$$\hat{Y} = b_i \cdot Y_i \tag{7}$$

 \hat{Y}^{ub} and \hat{Y}^{eq} indicate the composed species of the mixture in respectively unburnt and equilibrium state. The values of b_i are the result of the CSP method on the basis of a premixed laminar flame calculation. The reaction progress variable attains values between 0 (the unburnt mixed only state) and 1 (the equilibrium state).

The enthalpy scalar *i* is defined as:

$$i = \frac{h - h^{min}}{h^{ad} - h^{min}} = \frac{h - h^{min}}{V}$$
(8)

 h^{min} and h^{ad} indicate respectively the minimum and adiabatic enthalpy of the mixture. The enthalpy scalar moves between 0 (complete heat loss) and 1 (fully adiabatic).

Transport equations *c*, *f* and *i*

In order to use the CFI model in CFD simulations in combination with the transport equations 1-4, transport equations for the variables c, f and i have to be set up and Favre averaged.

If the CFI model is used for a simulation, each scalar in the problem is a function of the variables c, f and i. the ensemble Favre average of a scalar ψ is defined as:

$$\tilde{\psi} = \frac{1}{\bar{\rho}} \int_{c=0}^{1} \int_{f=0}^{1} \int_{i=0}^{1} \rho \psi(c, f, i) P(c, f, i) \, di \, df \, dc$$
(9)

The scalars *c*, *f* and *i* are assumed to be statistically independent, therefore the composed probability density function (*PDF*) P(c, f, i) can be simplified to:

$$P(c, f, i) = P(c)P(f)P(i)$$
(10)

For the reaction progress variable *c* and the mixture fraction *f* a $\beta - PDF$ is assumed. The parameters that determine the shape of a $\beta - PDF$ are the mean and the variance of the scalar to which the $\beta - PDF$ is applied. A single $\delta - PDF$, which is only characterized by the mean, will be used for the enthalpy scalar *i*. It is assumed that the enthalpy scalar is not much influenced by turbulent fluctuations (variances), unlike the reaction progress variable and mixture fraction, therefore a $\delta - PDF$ is sufficient.

The transport equations for *c*, *f* and *i* can be derived by rewriting equations 6-8 and inserting them in equations 3 and 4. After several assumptions and Favre averaging, the transport equations for the means of *c* (eq.12), *f* (eq.11) and *i* (eq.13):

$$\bar{\rho}\tilde{u}_{j}\frac{\partial\tilde{f}}{\partial x_{j}} - \frac{\partial}{\partial x_{j}}\left(\bar{\rho}D^{T}\frac{\partial\tilde{f}}{\partial x_{j}}\right) = 0$$
(11)

$$\frac{\partial \bar{\rho} \tilde{u}_{j} \tilde{c}}{\partial x_{j}} - \frac{\partial}{\partial x_{j}} \left(\bar{\rho} D^{T} \frac{\partial \tilde{c}}{\partial x_{j}} \right) \\
= \overline{S^{c}} - \overline{\left(\frac{W_{(i)}}{W} \right)} \overline{cS^{rad}} \\
+ \left(\overline{\left(\frac{W_{(ff)}}{W} \right)} \\
+ (1 - \tilde{i}) \overline{\left(\frac{W_{(i)}}{W} \right)} \overline{\left(\frac{V_{(ff)}}{V} \right)} \right) \bar{\rho} \tilde{c} \frac{\varepsilon}{k} \tilde{f}^{\tilde{\prime} \tilde{\prime} 2}$$
(12)

$$\frac{\partial \bar{\rho} \tilde{u}_{j} \tilde{\iota}}{\partial x_{j}} - \frac{\partial}{\partial x_{j}} \left(\bar{\rho} D^{T} \frac{\partial \tilde{\iota}}{\partial x_{j}} \right) = \bar{\rho} (\tilde{\iota} - 1) \left(\overline{\frac{V_{(ff)}}{V}} \right) \frac{\varepsilon}{k} \tilde{f}^{\prime \prime \prime 2} - \overline{S^{rad}}$$
(13)

Subscripted variables between parentheses in equations 11-13, for example $W_{(ff)}$, indicate differencing towards those variables.

In case of a fully premixed problem, which is the case in the experimental setup of this research, the transport equation for the means of c and i simplify to:

$$\frac{\partial \bar{\rho} \tilde{u}_j \tilde{c}}{\partial x_j} - \frac{\partial}{\partial x_j} \left(\bar{\rho} D^T \frac{\partial \tilde{c}}{\partial x_j} \right) = \overline{S^c} - \overline{\left(\frac{W_{(i)}}{W} \right)} \overline{c} \overline{S^{rad}}$$
(14)

$$\frac{\partial \bar{\rho} \tilde{u}_j \tilde{\iota}}{\partial x_j} - \frac{\partial}{\partial x_j} \left(\bar{\rho} D^T \frac{\partial \tilde{\iota}}{\partial x_j} \right) = -\overline{S^{rad}}$$
(15)

Chemical source term fitting

In figure 1 the source term of the progress variable c, S^c in equation 12, as calculated by the CFI model is depicted next to the results obtained on basis of detailed chemistry in a laminar flame calculation in Chemkin Premix. It can be observed that both the source term calculated by the CFI model and the detailed chemistry near equilibrium vanishes in equilibrium condition, c=1. Unfortunately the source term is severely under predicted by the CFI model in the range c=0.35-0.5 and severely over predicted for c=0.1-0.3. For c=0.0-0.1 the CFI model source term is set to 0 in order to prevent blowup and to bring it into the range of the detailed chemistry source term. The reason for this blowup lies in the steady state assumptions made in the CSP method. These are less, or not, valid for low cvalues, which correspond with low temperatures.

This insufficient prediction of the source term by the CFI model will lead to errors in the predicted evolution of the flame, and cannot be accepted. In order to remedy this, the source term for the reaction progress variable is obtained by fitting a parameterized expression for the chemical source term on basis of the source term as calculated for the premixed laminar flame at stoichiometric condition. These data are available anyway, as they are necessary for the optimization of the weight factors of the progress variable, b_i in equation 7, by the CSP method. For the chemical source term of the reaction progress variable the following parametric expression is used:

$$S^{c}(c,f) = A(f) \cdot c^{a} \cdot (1-c)^{b}$$
(16)

This expression satisfies the condition that the chemical source term of the progress variable vanishes at the unburnt (c=0) and the equilibrium (c=1) situation. The expression is always positive in this range of c and has one maximum value. The parameters a, b and A have been optimized for the best fit with the source term based on detailed chemistry in the premixed stoichiometric flame. The following values are found for this particular situation: a = 7.0261, b = 11.179 and A = 38250000. It must be noted that these values are dependent on the flame stoichiometry.

In figure 2 a comparison is made between the chemical source term of the reaction progress variable [kg m⁻³ s⁻¹] from the original CFI model, the Chemkin Premix laminar flame calculation and the analytic fit are shown. It can be seen that the analytic fit does not follow the Chemkin Premix source term perfectly, but it is a significant improvement over the original CFI model source term.

The most sensitive and important of the analytic fit is the value of A, which determines the magnitude of the maximum value of the source. This magnitude decreases fast with a deviation of the fuel to air ratio from stoichiometric. It is however not efficient to perform this fitting operation for a large number of different fuel to air ratios of laminar flames with detailed chemistry. These computations would require a large computational effort, which is next to that difficult to do without manual



Figure 1. CHEMICAL SOURCE TERM AS CALCULATED BY CFI MODEL AND CHEMKIN PREMIX AS FUNCTION OF THE REACTION PROGRESS VARIABLE C FOR A CERTAIN MIXTURE FRACTION.



Figure 2. CHEMICAL SOURCE TERM AS CALCULATED BY CFI MODEL AND CHEMKIN PREMIX AND FITTED SOURCE TERM AS FUNCTION OF THE REACTION PROGRESS VARIABLE *C* FOR A CERTAIN MIXTURE FRACTION.

interference. Therefore use is made of an empirical correlation for the stoichiometric dependence of the maximum magnitude of the chemical source term. It is assumed that the laminar flame speed scales similarly as the chemical source term with the fuel to air ratio. In that case the empirical data on laminar flame velocity can be used. A correlation well matching these data for laminar flame velocity depending on equivalence ratio, initial temperature and pressure is the Metghalchi and Keck expression [2]. This expression gives the dependence of the laminar burning velocity at reference condition s_L^0 as a function of the equivalence ratio:

$$s_L^0 = s_0^{max} \left(\frac{\Phi - \Phi_{\text{flam,l}}}{\Phi_{\text{max}} - \Phi_{\text{flam,l}}} \right)^a \left(\frac{\Phi_{\text{flam,r}} - \Phi}{\Phi_{\text{flam,r}} - \Phi_{\text{max}}} \right)^b$$
(17)

Where:

$$a = 2\left(\frac{\Phi_{\max} - \Phi_{\text{flam,l}}}{\Phi_{\text{flam,r}} - \Phi_{\text{flam,l}}}\right)$$
(18)

$$b = 2\left(\frac{\Phi_{\text{flam},r} - \Phi_{\text{max}}}{\Phi_{\text{flam},r} - \Phi_{\text{flam},l}}\right)$$
(19)

In above equations 17-19 the terms s_0^{max} , Φ_{max} , $\Phi_{flam,l}$ and $\Phi_{flam,r}$ are dependent on fuel. For application at other conditions than the reference conditions there is also a correlation available for the effect of initial temperature and pressure:

$$s_L = s_L^0 \left(\frac{T_u}{T_{ref}}\right)^{\alpha} \left(\frac{p}{p_{ref}}\right)^{\beta}$$
(20)

In equation 20 α and β are dependent on the equivalence ratio with an empirically determined second order polynomial expression.

Equation 16 displays similarities with the expression for the mean chemical source term in the Bray-Moss-Libby (BML) model [15]. In the BML model the chemical source term has the same dependency on c, $c^a \cdot (1-c)^b$ with a=1 and b=1, and is also a function of the laminar burning velocity.

Radiative heat loss

As mentioned before, under the conditions the setup operates a significant amount of soot formation is expected. The soot also has an influence on the enthalpy of the flow because the soot particles are radiating. The radiative heat loss term S^{rad} in the enthalpy scalar *i* transport equation 15 therefore not only consists of a gaseous radiative part, but also a soot particle part:

$$S^{rad} = S^{rad,gas} + S^{rad,soot}$$
(21)

The gaseous radiation model that is implemented assumes that every volume of gas radiates to a wall of constant temperature and the gas is optically thin. The influence of the geometry is left out of consideration. The term $S^{rad,gas}$ now only depends on temperature and species concentrations. The theory of the model can be found in [3]. According to this theory $S^{rad,gas}$ can be calculated with the following expression, if it is assumed that CO₂ and H₂O are the main radiating species:

$$S^{rad,gas} = 4 \cdot P \cdot \left(a_{P,CO2} \cdot X_{CO2} + a_{P,H2O} \cdot X_{H2O}\right) \cdot \sigma$$
$$\cdot T^4 \ [W/m^3]$$
(22)

The coefficients $a_{P,CO2}$ and $a_{P,H2O}$ can be calculated with the following expression:

$$log_{10}\left(\frac{a_{P,i}}{a_{P,i,ref}}\right) = \sum_{n=0}^{6} a_{i,n} \left(\frac{T}{300}\right)^{n}$$
(23)

(24)

Where:

$$a_{P,i,ref} = 1/(m \cdot atm)$$

The coefficients $a_{i,n}$ are presented in table 1.

Coefficient	CO ₂	H ₂ O	
a0	0.22317E01	0.38041E01	
a1	-0.15829E01	-0.27808E01	
a2	0.13296E01	0.11672E01	
a3	-0.50707E00	-0.28491E00	
a4	0.93334E-01	0.38163E-01	
a5	-0.83108E-02	-0.26292E-02	
a6	0.28834E-03	0.37774E-04	

Table 1.

The soot particle radiation can be calculated with the following expression:

$$S^{rad,soot} = 4 \cdot C_{sootrad} \cdot \sigma \cdot f_s \cdot T \\ \cdot \left(T^4 - T^4_{wall}\right) \left[W/m^3\right]$$
(25)

Where:

$$f_s = Ys\frac{\rho}{\rho_s} \tag{26}$$

And:

 $\begin{array}{l} P = \text{pressure [bar]} \\ a_{P,i} = \text{mean absorption coefficient of species i} \\ X_i = \text{molar fraction species i} \\ \sigma = \text{Stefan-Boltzmann constant [W/m² · K⁴]} \\ T = \text{temperature [K]} \\ C_{sootrad} = \text{soot radiation constant [1/m · K]} \\ f_s = \text{soot volume fraction} \\ T_{wall} = \text{reactor wall temperature [K]} \end{array}$

This method of modeling soot particle radiation was also used in the research of Albrecht [4].

Soot formation modeling

In this section a simplified model of soot formation based on the processes of nucleation, surface growth, agglomeration and oxidation, is presented. As mentioned before, the CFI combustion model describes the gas phase chemistry and therefore provides the concentrations of gaseous species in the combusting flow field, under which acetylene (C_2H_2), oxygen (O_2) and hydrogen (H_2) The soot nucleation and surface growth are linked to the gas phase chemistry by the assumption that acetylene is the indicative species for the locations in the flame where nucleation and soot Copyright © 2011 by ASME mass growth occurs [5][6][7][8]. Nucleation is described by a first-order function of acetylene concentration. Surface growth is modeled with the HACA mechanism [9][10][11]. Particle agglomeration is modeled by the normal square dependence in the free molecular regime [6][7][8]. Soot oxidation by O_2 and OH was treated as in [8] and soot oxidation by CO2, H2O and H2 was evaluated using [12].

The soot model involves the solution of two transport equations for the soot mass fraction Y_s and the soot particle number density N_s :

$$\bar{\rho}\tilde{u}_{j}\frac{\partial\tilde{Y}_{S}}{\partial x_{j}} - \frac{\partial}{\partial x_{j}}\left(\left(\bar{\rho}D_{Y_{S}} + \frac{\mu_{T}}{Sc_{Y_{S},T}}\right)\frac{\partial\tilde{Y}_{S}}{\partial x_{j}}\right) = \overline{S_{Y_{S}}}$$
(27)

$$\bar{\rho}\tilde{u}_{j}\frac{\partial\widetilde{N_{S}}}{\partial x_{j}} - \frac{\partial}{\partial x_{j}}\left(\left(\bar{\rho}D_{N_{S}} + \frac{\mu_{T}}{Sc_{N_{S},T}}\right)\frac{\partial\widetilde{N_{S}}}{\partial x_{j}}\right) = \overline{S_{N_{S}}}$$
(28)

 $\rho = mixture density$

 $\begin{array}{l} u_{j} = \text{velocity component} \\ D_{Y_{S}} = \text{molecular diffusion coefficient for } Y_{S} \\ D_{N_{S}} = \text{molecular diffusion coefficient for } N_{S} \\ \mu_{T} = \text{turbulent viscosity} \\ Sc_{Y_{S},T} = \text{turbulent Schmidt number for } Y_{S} \\ Sc_{N_{S},T} = \text{turbulent Schmidt number for } N_{S} \end{array}$

The source terms S_{Y_S} and S_{N_S} in equations 27 and 28 are in their non-averaged form:

$$S_{Y_S} = \alpha_{Y_S} + \beta_{Y_S} Y_S^{2/3} N_S^{1/3} + \gamma_{Y_S} Y_S$$
(29)

$$S_{N_S} = \alpha_{N_S} + \beta_{N_S} Y_S^{1/6} N_S^{11/6}$$
(30)

Where:

1

$$\alpha_{Y_S} = 2w_{nu}W_C \tag{31}$$

$$\mathcal{B}_{Y_{S}} = \{ w_{sg} - [(w_{ox,O_{2}} + w_{ox,OH})W_{C} + w_{ox,CO_{2}} + w_{ox,H_{2}O}] \} \pi \rho \left(\frac{6}{\pi \rho_{S}}\right)^{2/3}$$
(32)

$$\gamma_{Y_S} = -w_{ox,H_2}\rho \tag{33}$$

$$\alpha_{N_S} = 2w_{nu} \frac{N_A}{N_{C,min}}$$
(34)

$$\beta_{N_S} = -2C_{S,pa} \left(\frac{6}{\pi\rho_S}\right)^{1/6} \left(\frac{6\sigma_B T}{\rho_S}\right)^{1/6} \rho^2$$
(35)

And:

$$\begin{split} & w_{nu} = \text{nucleation rate} \\ & W_{C} = \text{carbon molar mass} \\ & w_{sg} = \text{surface growth rate} \\ & w_{ox,[species]} = \text{reaction rate of soot oxidation by [species]} \\ & \rho = \text{mixture density} \\ & \rho_{S} = \text{soot density} \\ & N_{A} = \text{Avogadro number} \\ & N_{C,min} = \text{number of carbon atoms in the incipient soot} \\ & \text{particle} \\ & C_{S,pa} = \text{agglomeration constant} \\ & \sigma_{B} = \text{Stefan-Boltzmann constant} \end{split}$$

T = temperature

The nucleation rate w_{nu} in equation 31 is given by:

$$w_{nu} = k1[C_2H_2]$$
(36)

The surface growth w_{sg} in equation 32 is given by:

$$w_{sg} = \alpha_{FW} \frac{2W_{C}}{N_{A}} \frac{k_{2,f} k_{4}[H][C_{2}H_{2}][C_{soot} - H]}{k_{2,b}[H_{2}] + k_{3}[H] + k_{4}[C_{2}H_{2}]}$$
(37)

The term α_{FW} in equation 37 is an empirical factor of order unity. In [10] the best correlation of w_{sg} with experimental data was obtained for the following expression for α_{FW} :

$$\alpha_{FW}(T) = 0.00115 \cdot e^{\frac{12500}{T}}$$
(38)

The coupling of the soot model with the CFI combustion model and the CFD simulations is done via the mixture temperature, density and the species concentrations of C2H2, O2, OH, CO2, H2O and H2. In order to obtain the variables soot mass fraction Y_s and the soot particle number density N_s the two transport equations 27 and 28 have to be solved.

EXPERIMENTAL SETUP

In order to demonstrate the production of syngas on basis of natural gas and air or Nitrox (air enriched to 40 vol % oxygen) by ultra rich combustion a test rig was built at the University of Twente. The layout of the setup is shown in figure 3 on the next page. Natural gas is supplied to the test rig by a 10 bar compressor (7) fed by the gas network. The natural gas flow is mixed in the mixer manifold (10) with an air flow delivered by a 10 bar



air compressor (5) and an oxygen flow delivered by a set of bottles (3). All mass flows are individually set by mass flow controller valves. The mix of air, oxygen and natural gas is heated subsequently to 673 K in a shell and tube heat exchanger (12), by a 703 K air flow. The hot mix of reactants is fed to the reactor (13). A cross section of the reactor is sketched in figure 4.



The premixed preheated natural gas/air/oxygen flows through a perforated plate to a radial slot swirler. The swirled gas enters at high velocity (to prevent flame flash back) through an annular passage into the cylindrical reactor chamber of diameter (d) 100 mm and length (l) 500 mm. Due to the expansion in diameter, the swirled gas is swept to large radius and induces a central recirculation area at the axis. This hot recirculating flow stabilizes the ignition of the reactants. At start up the recirculating flow is ignited by a spark plug located at the burner mouth. The reactor has ceramic lined walls with very low heat loss. The nominal average residence time has an approximate value of 50 ms. At the exit of the reactor the extremely hot syngas flow is cooled in a shell and tube heat exchanger (15) by a water flow to an intermediate temperature of 1023 K. In the second cooler (17) the syngas flow was cooled further down to 313 K by a second shell and tube heat exchanger by a water flow. Subsequently the syngas flow is throttled in a valve (21) to atmospheric pressure and discharged safely into the atmosphere by combustion in a flare (13). Hence the reactor pressure is controlled by the throttle valve.

In this research measurements will be done on the setup operating at pressures from 1 to 6 bar and at equivalence ratios 2 to 4. The goal of the experiments is to validate the numerical combustion and soot formation model discussed in the previous section.

When the setup is in operation, a continuous flow of sample will be extracted from the reactor at three different axial and radial points. This flow has to be chemically quenched and diluted very rapidly in order to avoid chemical composition change and soot particle growth and coagulation. Before the dilution step it will be possible to analyze the gas composition with a gas chromatograph and after the dilution step the soot concentration and size distribution will be measured with a Scanning Mobility Particle Sizer.

Experiments form previous work

Previous experiments with a very similar setup and under the same conditions were done by Albrecht *et al.* [14]. The results from the CO concentration measurements (dried product gas) for several equivalence ratios of Nitrox/natural gas mixtures are shown in figure 5. Also shown in figure 5 are the results from Chemkin Premix and Chemkin PSR calculations.



Figure 5. COMPARISION OF MEASURED AND PREDICTED CO CONCENTRATION IN SYNGAS PRODUCED ON BASIS OF NATURAL GAS/NITROX.

Table 2 gives the measured species concentrations at an equivalence ratio Φ of 3 and their values at 50 ms in Chemkin PSR, Chemkin Premix and chemical equilibrium calculations.

From the measured data shown in figure 5 and table 2 it can be concluded that the mole fraction of CO in the produced (dried) syngas is approximately 0.16. In the database of the CFI model this CO mole fraction of 0.16 corresponds for a Nitrox/natural gas mixture at Φ =3 with a reaction progress variable value of c=0.55. Therefore equilibrium (c=1) is not reached in the reactor. This is shown in figure 6.

Also shown in figure 6 is the chemical source term S^c as function of the reaction progress variable. The solid vertical line and the arrow show that for a reaction progress variable of c = 0.55 the fitted chemical source (see previous section) has a value of approximately 75. This is an indication that the mixture would move more in the direction of equilibrium if the residence time in the reactor would have been longer.

	H2	CO	CH4	CO2	C2H2
Measured	30.6	16.4	5.0	3.6	7.0
PSR	29.7	16.0	5.6	3.3	4.5
@ 50 ms					
Premix	32.7	14.9	4.2	3.2	5.4
@ 50 ms					
Equilibrium	44.3	24.1	0	1.5	0

Table 2.MEASURED AND PREDICTED SPECIESCONCENTRATIONS [VOL %] IN DRIED PRODUCEDSYNGAS

The observation that the mixture in the reactor does not reach equilibrium, but only reaches a reaction progress variable of c=0.55, emphasizes the need of a accurate chemical source term prediction in the lower c-range. The development of the chemical source term from the original CFI model, see figure 2, would have over predicted the chemical activity severely. The analytic fit approaches the chemical source term development of the detailed Chemkin Premix calculation significantly better.



Figure 6. MOLE FRACTION CO FOR DRIED SYNGAS, LEFT VERTICAL AXIS AND SOLID LINE, AND FITTED SOURCE TERM, RIGHT VERTICAL AXIS AND DASHED LINE, AS FUNCTION OF THE REACTION PROGRESS VARIABLE FOR EQUIVALENCE RATIO 3 NITROX/NATURAL GAS.

CONCLUSIONS AND DISCUSSION

In this paper the CFI combustion model, developed at the Laboratory of Thermal Engineering of the University of Twente, is discussed. This turbulent combustion model is capable of modeling the mixing of fuel, detailed chemistry and heat loss in turbulent combustors accurately with a limited number of transport equations.

Fitting of the Chemkin Premix chemical source term of the reaction progress variable is a significant improvement over the source term calculated by the CFI model.

Combination of radiation and soot formation models with the CFI combustion model will give a complete picture of the processes in the partial oxidation reactor.

A comparison of the results of previous experiments and the database of the CFI model show that equilibrium is not reached in the reactor. This emphasizes that a combustion modeled with detailed chemistry, like the discussed CFI model, is necessary in order to predict the non-equilibrium conditions.

In this paper an overview is given of the ultra rich combustion setup that is present at the Laboratory of Thermal Engineering of the University of Twente.

The planned experiments will give valuable validation data for the performance of combustion and soot formation models at ultra rich conditions that are not yet available in literature.

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NOMENCLATURE

P = pressure [bar] $a_{P,i} =$ mean absorption coefficient of species i

 $X_i =$ molar fraction species i

- $\sigma =$ Stefan-Boltzmann constant [W/m² · K⁴]
- T =temperature [K]
- $C_{sootrad}$ = soot radiation constant [1/m · K] f_s = soot volume fraction
- T_{wall} = reactor wall temperature [K]
- $\rho = mixture density$
- $u_i =$ velocity component
- D_{Y_S} = molecular diffusion coefficient for Y_S
- D_{N_s} = molecular diffusion coefficient for N_s
- μ_T = turbulent viscosity
- $Sc_{Y_{S},T}$ = turbulent Schmidt number for Y_{S}
- $Sc_{N_S,T}$ = turbulent Schmidt number for N_S
- $w_{nu} =$ nucleation rate
- $W_{\rm C}$ = carbon molar mass
- w_{sg} = surface growth rate

 $w_{ox,[species]}$ = reaction rate of soot oxidation by [species]

- $\rho = mixture density$
- $\rho_s = \text{soot density}$
- $N_{A} = Avogadro number$

 $N_{C,\min}^{n}$ = number of carbon atoms in the incipient soot particle

 $C_{S,pa}$ = agglomeration constant

- $\sigma_{\scriptscriptstyle B} = \text{Stefan-Boltzmann constant}$
- T = temperature

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