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Potentials for Usage of Significantly Reduced Chemical Mechanisms in Numerical Modeling of Combustion Processes

The paper presents comparison of the results obtained in numerical research conducted, with the aim to simulate combustion of methane-based fuels like natural gas, Serbian gas, biogas, etc. Presented results were obtained using experimentally verified, full chemical mechanism GRI 3.0, with 325 chemical reactions, and using selected, very reduced chemical mechanism, with only two chemical reactions, based on two-step C.K. Westbrook & F.L. Dryer (WD) model. "ChemKin" software was used for all numerical simulations of chemical kinetics and "Fluent" for CFD analysis. The goal was to determine possibilities and application fields of this very reduced chemical mechanism in CFD calculations, especially in cases when flows with chemical reactions, through complex geometry of burners and furnaces, disable usage of full mechanisms.

Keywords: numerical simulation of combustion process, reduced chemical mechanisms, combustion modeling.

1. INTRODUCTION

Modern computer systems and development of specialized software packages, allow wider usage of numerical based methods for different combustion processes modeling. For these complex processes, each year sets up higher and higher modern standards for environment protection, pollutant emission limits, higher energy efficient devices, etc.

Theoretically, powerful computer systems together with adequate software capable to solve a huge number of equations based on appropriate input data, can resolve a wide range of different problems in combustion. In practice, even relatively simple problems are very often a serious barrier for successful numerical simulation. Adequate combustion modeling is very complicated, because of the complexity of combustion process, which includes many main and intermediate chemical reactions, formatting and decomposing of main and intermediate species (chemical compounds), often with a very short life time, in less than a millimeter thin layer of flame front. In addition, combustion process always includes fast temperature, density and volume changes, which involve chemical transformations of inlet matter, often followed by turbulent flow in complex geometry. Only by understanding each of these phenomena, separately

adequate and appropriate numerical modeling of combustion processes can be established.

During three years of European FP6 project FlexHEAT, (Flexible Premixed Burners for Low-Cost Domestic Heating Systems), Combustion Laboratory at Faculty of Mechanical Engineering in Belgrade participated as the coordinator of the project for numerical modeling and CFD analysis. One of the main goals was to create numerical model, to solve chemical kinetics and CFD model of flow, with chemical reactions for the process of natural gas combustion.

The atmospheric premixed burner, manufactured by Holland company "BCT", (which also participated in the project), was a starting point during the project. Development of the burner was the main goal of the project. As a part of this main goal, different optimizations of the burner had to be made. Some of several subtasks were: expansion of dynamic range, reduction of pollutant emission (NO_x and CO), adaptation of burner for combustion of different, (lower quality) fuels, like Serbian gas or biogas, etc. Before the final experimental research, for each of these subtasks a theoretical overview, numerical, and physical modeling, were performed.

Numerical software "ChemKin", of Reaction Design – USA, and "Fluent", of ANSYS – USA, were used for the numerical modeling of the process. "ChemKin" was used for modeling of chemical kinetics of combustion process, while "Fluent" was used for CFD analysis.

One of the key elements was the burner mantle design. Under this subtask, burner shape, pattern of mantle, dimensions and flame holes arrangement were optimized. Complex structure of flame holes pattern,

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furnace and burner geometry made CFD modeling, complicated and inefficient when full chemical mechanisms, like GRI-Mesh 3.0, SNL, SD and others, were used [1].

2. MAIN RESEARCH

Real combustion process scheme, even for simplest possible CH fuel like methane (CH₄), is too complex and must be reduced for practical use. One of the several simplified schemes of CH₄ combustion, shown in Figure 1 consists of about 30 chemical species and about 50 chemical reactions, and although quite complex, it doesn't even include NO_x formation mechanisms.

Results of the preliminary research show that reduced chemical mechanism always gives lower disturbance of final solution for CFD calculation than simplifications of numerical grid or model geometry. Reducing grid density or simplifying geometry of the model has significant influence on the solution. On the other hand, there is no need to precisely determine concentrations of some short lifetime chemical species whose effect is insignificant, Figure 1.

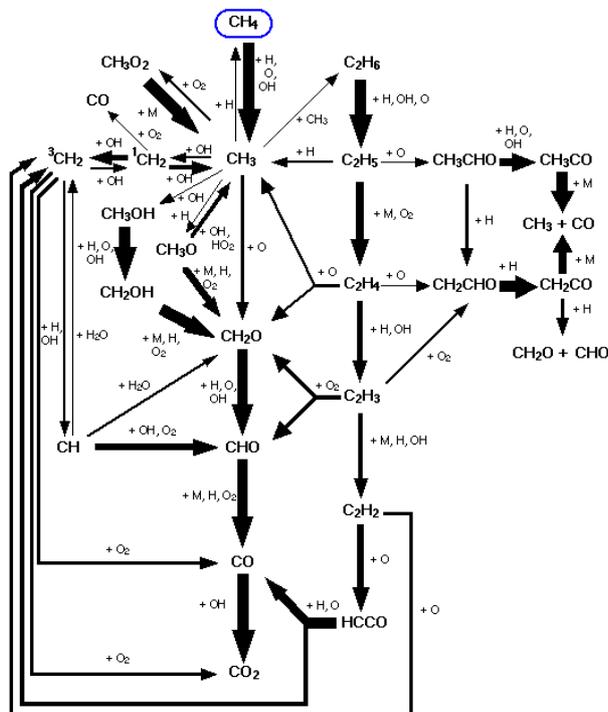


Figure 1. Simplified scheme for CH₄ combustion

This figure shows one of the numerous ways to simplify real CH₄ combustion process. Although complex, the presented scheme has less species and chemical reactions than the full chemical mechanisms. CFD calculation with full mechanism is often impossible even for state-of-the-art computers. That is the main reason to reduce chemical mechanism.

2.1 Research goals

The main tasks presented in this paper were:

1. selection of simple chemical model for CH₄ combustion and creating adequate chemical mechanism, in the form acceptable for numerical software, based on selected chemical model,

2. main species, axial velocities and temperature distributions, for CH₄/Air combustion,
3. finding limitations and application domain for selected reduced chemical mechanism,
4. validation of obtained results, through comparison with results obtained using full referent chemical mechanism, results from literature and experimental results.

One of the leading ideas of significantly reduced chemical mechanism is to simplify selecting the numerical model and CPU calculation time for combustion numerical simulation and to preserve solution correctness and reliability. The main results expected from CFD calculation, from the chemical kinetics point of view, were velocities, temperature distributions and distribution of main pollutant species.

2.2 Basic principles of mechanism selections

Developing reduced chemical mechanism is iterative procedure, which has to satisfy limiting conditions for every iterative step. Heuristic approach was used in this particular case. Validation of the results for tested reduced mechanisms was based on three key parameters:

1. temperature profiles,
2. axial velocity profiles and
3. concentration profiles for CO, CO₂, O₂, H₂O.

After validation of the obtained results, based on the mentioned three key parameters, the final testing was done using combination of "Fluent" software and selected reduced chemical mechanism.

2.3 Selection of referent mechanism

The GRI 3.0, developed by Gas Research Institute at Berkley University, has been selected as a referent mechanism. The mechanism was designed for numerical simulation of combustion of C₁ to C₃ fuels. It consists of 5 chemical elements (C, O, H, N and Ar), 53 chemical species and 325 chemical reactions [2].

Results for methane combustion, obtained using this mechanism were tested experimentally at Combustion Laboratory, Faculty of Mechanical Engineering in Belgrade.

2.4 Selection of reduced model

Based on the preliminary research, a two step C.K. Westbrook & F.L. Dryer (WD) model [3] for CH₄ combustion was selected as simplest and best of all preliminary tested models. The model consists of two chemical reactions (1) and (2), where reaction (2) is reversal.



The first chemical reaction (1) treats formations of water vapor (H₂O) and carbon monoxide (CO), while the second chemical reaction (2) treats oxidation of carbon monoxide to carbon dioxide (CO₂) and its dissociation.

This reduced model covers CO, CO₂ and H₂O formation.

2.5 Reduced WD chemical mechanism construction

Chemical mechanism in the form of input data for numerical software for combustion chemistry modeling usually has at least three parts. Most important of all is Gas Phase Kinetic File. This part of chemical mechanism is practically a list of all chemical reactions of interest to simulation including appropriate Arrhenius equation coefficients. The second part of the chemical reaction mechanism is Thermodynamic Data Base, which includes thermodynamic coefficients for all chemical species used in Gas Phase Kinetic File. The third part of the chemical reaction mechanism is usually Transport Data file, consisting of transport data, like Lennard-Jones diameter of Lennard-Jones potential, etc., for species used in Gas Phase Kinetic File.

Gas Phase Kinetic file, made for selected significantly reduced mechanism, as a key part of chemical reaction mechanism, had several modifications during research. Final evolution of this reduced mechanism later used in numerical software for chemical kinetics "ChemKin" is given in the following list:

```
ELEMENTS
C H O N
END
SPECIES
CH4 O2 CO H2O CO2 N2
END
REACTIONS KCAL/MOLE
CH4+1.5O2=CO+2H2O 2.8E+9 0.00 48.4
FORD /CH4 -0.3/
FORD /O2 1.3/
CO+0.5O2=>CO2 10.00E+14 0.00 40
FORD /H2O 0.5/
FORD /O2 0.25/
REV /5E+8 0.000 40/
END
```

Three coefficients, given for each equation as a bold text, are values of Arrhenius equation (3) coefficients, (respectively): pre-exponential factor A_i , temperature coefficient β_i , and activation energy E_i .

$$k_{fi} = A_i T^{\beta_i} \exp\left(\frac{-E_i}{R_c T}\right) \quad (3)$$

Presented Gas Phase Kinetic File together with adequate Thermodynamic Data Base and Transport Data file were used for further numerical simulation as reduced WD chemical reaction mechanism.

2.6 Numerical modeling of the problem

During the research, three different models were used: Equilibrium, Premixed Laminar Burner Stabilized Flame and Premixed Laminar Flame Speed Calculation Model. Presented results were obtained for Methane/Air combustion and for different values of air ratio coefficients λ [2].

First, calculations were done using the Equilibrium model with input data (used for both tested mechanism WD and GRI 3.0) [1]:

- Constant system pressure (p),
- $T_{init} = 300$ K – Inlet gas and air temperature,
- $p_{sis} = 101.325$ kPa – System pressure,
- $T_{end} = 2100$ K – Predicted outlet temperature, etc.

15 different mixtures with different values of air ratio coefficient λ , from $\lambda = 1.43$ to $\lambda = 0.77$ were tested. Results for this model were successfully obtained for both tested mechanisms. A part of these results is presented in Figures 2-11. Comments and conclusions related to these results are given at the end of this article.

The next set of simulations is completed using the Premixed Laminar Flame Speed Calculation model. As results of these simulations, graphs of axial velocities distributions were obtained, for different values of air ratio coefficients. This set of simulations was also done for both tested mechanisms, significantly reduced WD mechanism and referent full GRI 3.0.

During the set up of the simulation for GRI 3.0 chemical mechanism, fixed number of six numerical points is used for first iteration, with adequate iterative grid refinement. Initial temperature profile is given over 12 temperature points with necessary adjustments for each case and each value of air ratio coefficient. In the problem set up, three iterative cycles were given, with numerical grid refinement controlled over adaptive grid control based on solution gradient and adaptive grid control based on solution curvature. Calculation domain was from $L_1 = 0$ to 0.35 cm, for the first iteration, to $L_3 = -2$ to 10 cm, for the last iteration, where L is a distance from the zero (referent) plane of flame.

The results of the simulation, using Equilibrium model, showed good correlations of the WD and GRI chemical mechanisms only for $\lambda \geq 1$. For simulation in Premixed Laminar Flame Speed Calculation model, the values of $1.0 \leq \lambda \leq 1.5$ were used.

As for the WD two-step mechanism, set up of the simulation was done using predefined numerical grid of 7 points fixed to specific distances, instead of fixed number of points. Doing so, numerical grid was more adapted to the problem for a first iteration by putting more of the grid points in the first millimeter of the flame front i.e. in the part of the domain with most intensive chemistry. Initial temperature profile for WD mechanism testing was given in this case, over each of seven grid points. Profiles were adapted for every new calculation i.e. for each used λ value.

Initial value of mass flow for both tested mechanisms was set to $m = 0.046$ g/cm²s, and for a referent point i.e. "Fixed Temperature to constrain flame position", point with temperature of $T_{fix} = 400$ K was selected.

For both used chemical mechanisms, stable solutions were obtained, but while testing WD two-step chemical mechanism, stability of the solution was dependent of initial parameter set up. A part of the obtained results is presented in Figures 5, 6, and 7 followed by comments and conclusions for this part of research.

The final part of numerical simulations was performed using Premixed Laminar Burner Stabilized Flame model, with the aim to calculate main species distribution for different values of λ . Input values were the same as for the previous simulation. The results were in very good agreement but CPU time needed for this calculation was more than 100 times longer for second type of the problem. Air ratio coefficient for this simulation was also in the range of $1.0 \leq \lambda \leq 1.5$. Some of the results are given in Figures 8-11.

2.7 Results

The results (for Equilibrium model), are presented in Figures 2-4. As for the maximal adiabatic flame temperature, significantly reduced WD two-step chemical mechanism shows good correspondence with full GRI 3.0 chemical mechanism for the whole λ domain. The equilibrium concentrations of main species of interest for WD two-step mechanism and different values of air ratio coefficient λ , show good agreement with GRI 3.0 for stoichiometric ($\lambda = 1$), and lean ($\lambda > 1$) combustion, as it can be seen in Figure 3.

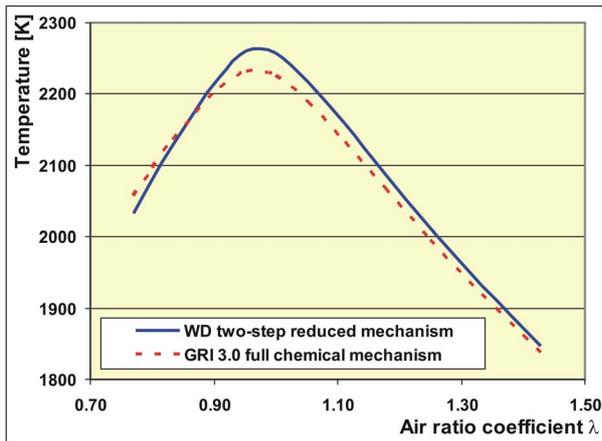


Figure 2. Comparison of results for maximal adiabatic flame temperatures for WD and GRI 3.0 mechanisms

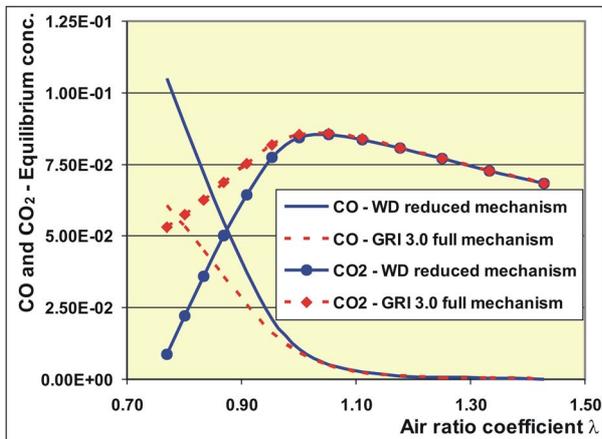


Figure 3. Comparison of results for CO and CO₂ equilibrium concentrations for WD and GRI 3.0

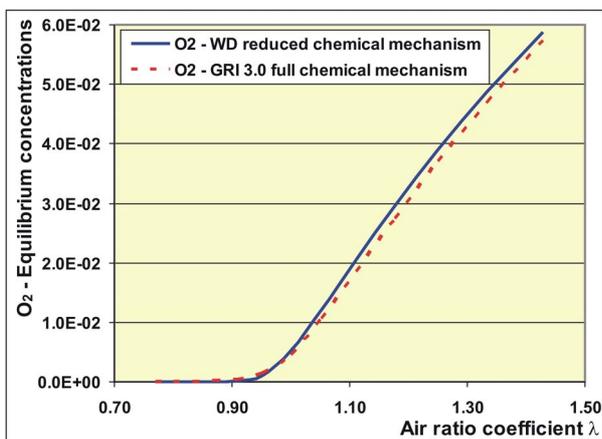


Figure 4. Comparison of results for O₂ equilibrium concentrations for WD and GRI 3.0 and different λ values

The aim of the second part of the research was to determine quality of significantly reduced chemical mechanisms, like two-step WD, for axial velocity profiles calculations. The results presented in Figures 5, 6, and 7 are in good agreement with full mechanism. It is important to notify that the object of this project, atmospheric BCT burner, is designed for maximal thermal power of about 10.2 kW. At this nominal value of thermal power, air ratio coefficient is about $\lambda = 1.3$. This is a theoretical value, but in practice, the range for air ratio coefficient is between $1.20 \leq \lambda \leq 1.30$. Representative diagrams for axial velocity profiles are given in Figures 5-7.

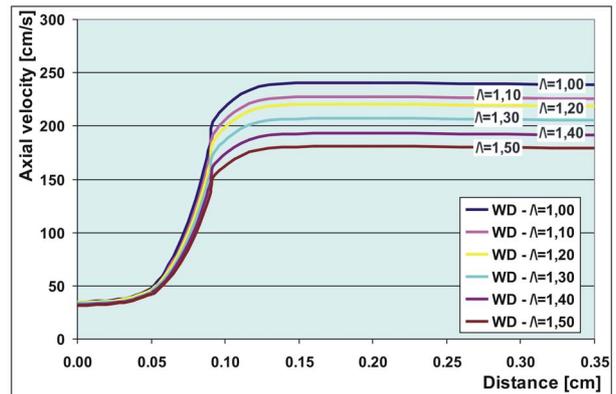


Figure 5. Axial velocities profiles for WD mechanism

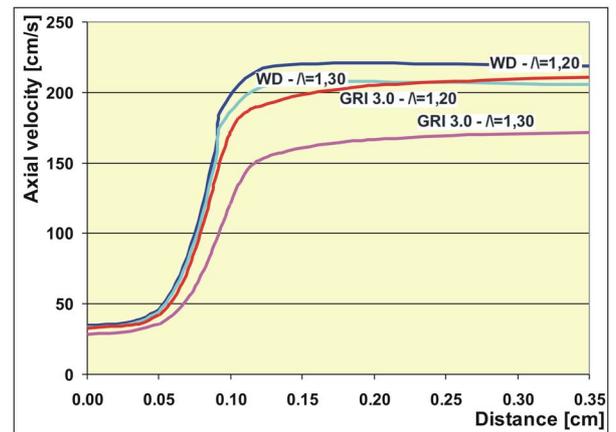


Figure 6. Comparison of axial velocity profiles for WD and GRI 3.0 reduced mechanisms for $\lambda = 1.2$ and $\lambda = 1.3$

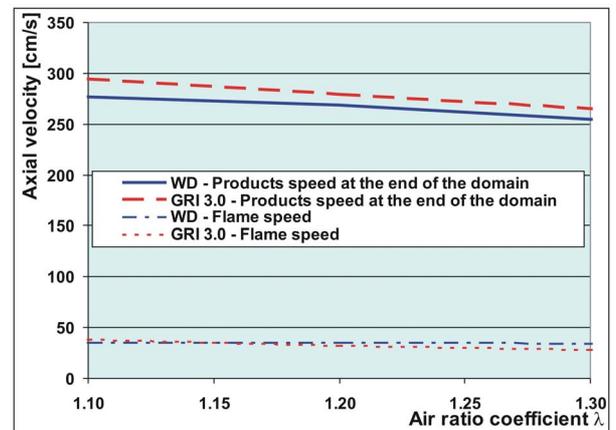


Figure 7. Comparison of flame speeds and combustion products speed at the end of domain for WD and GRI 3.0

Flame speed calculations using WD mechanism, shows that calculated flame speed has correct values

compared with GRI 3.0 results, and axial velocities profiles have adequate shape and values, especially for values from the range of $1.2 \leq \lambda \leq 1.4$. As a result, for lean mixtures with $\lambda > 1.5$, differences between results obtained using WD and GRI mechanisms become pronounced.

Further numerical research was concerned with main species concentration profiles. Some of the representative results are presented in this paper. The presented results are given for different air ratio coefficients Figures 8-11.

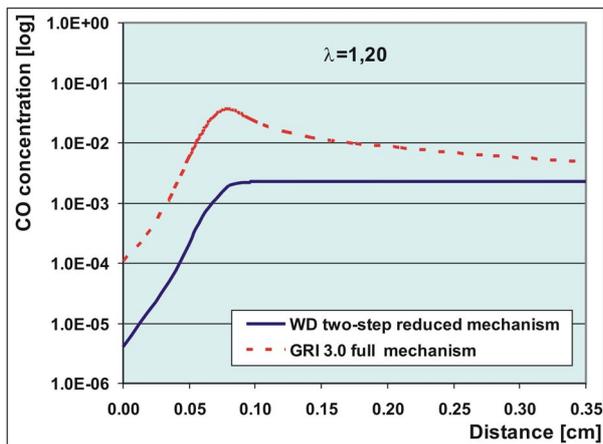


Figure 8. Comparison of CO concentration profiles for WD and GRI 3.0 chemical mechanism and for $\lambda = 1.20$

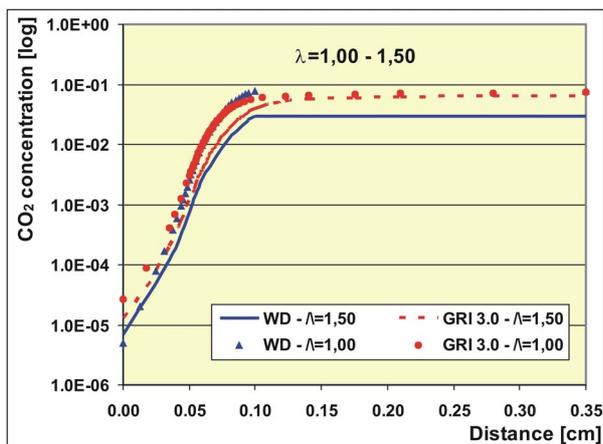


Figure 9. Comparison of CO₂ concentration profiles for WD and GRI 3.0, and for λ values: $\lambda = 1.00$ and $\lambda = 1.50$

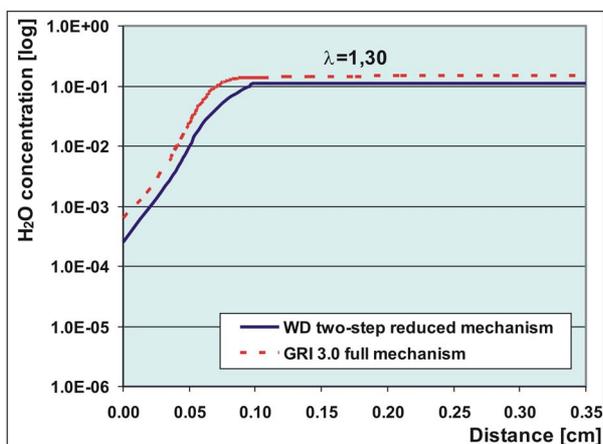


Figure 10. Comparison of H₂O concentration profiles for WD and GRI 3.0, and for $\lambda = 1.30$

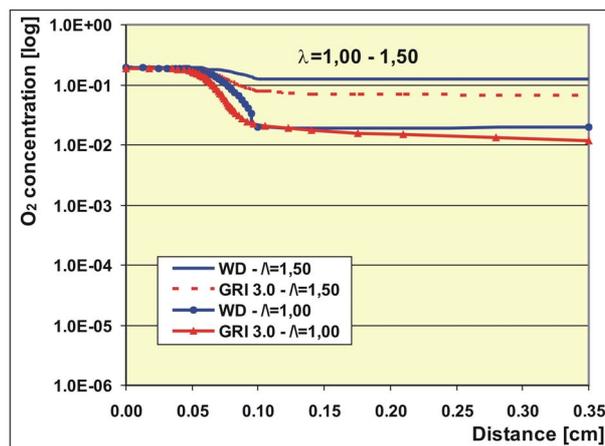


Figure 11. Comparison of O₂ concentration profiles for WD and GRI 3.0, and for λ values: $\lambda = 1.00$ and $\lambda = 1.50$

Reduced WD chemical mechanism treats five chemical compounds. Besides the presented diagrams for CO and CO₂, WD mechanism gives CH₄, O₂ and H₂O concentration profiles for combustion products, which is often enough for practical purposes.

The final part of this research was validation of the WD mechanism through CFD software package “Fluent”. CFD results obtained using WD reduced mechanism are not a subject of this paper, but with a purpose of visual validation and as helpful for some conclusions, some of the CFD results are presented in Figures 12-15. The object was, as already explained 10.2 kW atmospheric, premixed burner.

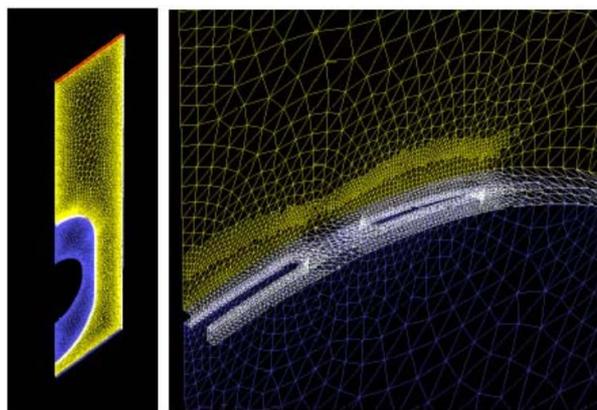


Figure 12. Detail of CFD grid in reaction zone above flame ports

Using the reduced chemical mechanism and a high-density numerical grid, gave stable and precise solutions, as shown in Figure 12.

Figure 13 confirms well calculated temperature distribution over BCT burner mantle, with maximal flame temperature of about 2000 K, as expected and calculated during the simulations using “ChemKin”, software.

The results obtained for CO concentration distribution in flame are also in agreement with the expected and earlier calculated ones. As it can be seen in Figure 14 2D distribution of CO in CH₄/Air flame for nominal thermal load of BCT burner of 10.2 kW, concentration of CO in flame zone is in the range of $3.0 \cdot 10^3$ to $3.5 \cdot 10^3$, as it has been calculated using “ChemKin”.

Figure 15 shows experimental validation of the predicted flame shape and position using WD mechanism. At the left side of the picture is CFD

prediction of flame shape and form, and at the right side is actual flame for nominal thermal load.

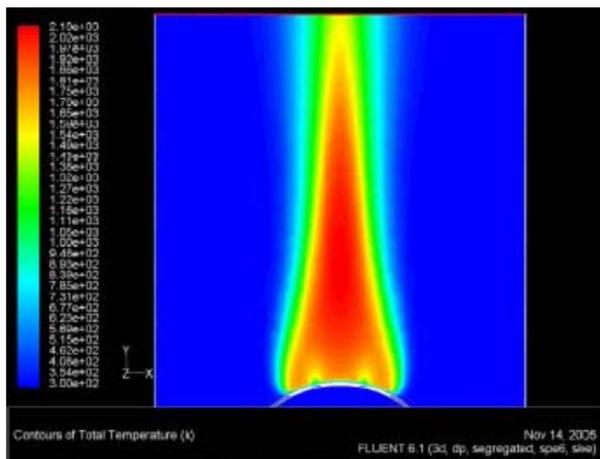


Figure 13. Temperature distribution for BCT burner during CH₄ combustion as a result of CFD analysis based on WD mechanism

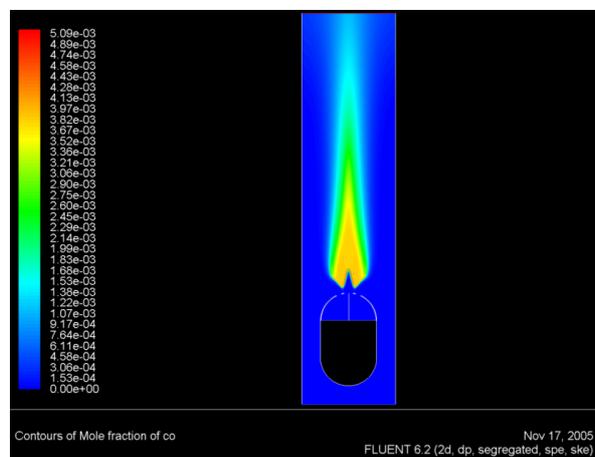


Figure 14. CO concentration distribution over BCT burner as a result of CFD analysis based on WD mechanism



Figure 15. Comparison of flame shape obtained using WD based CFD calculation (in the middle), and photo of the flame (at the right)

The CFD calculations were stable with relatively short CPU time and yet the significantly reduced WD chemical mechanism gave very useful results.

3. COMMENTS AND CONCLUSIONS

Significantly reduced C.K. Westbrook & F.L. Dryer CH₄ combustion model was selected as a base. For this

model, adequate reduced chemical reaction mechanism together with all necessary files was prepared as input data form for “ChemKin” numerical software. The results for species concentrations and flame speed were obtained for lean methane/air mixtures.

Together with these results, under the same initial conditions, the results using GRI 3.0 as a validation (referent) chemical mechanism were obtained. The obtained results using WD mechanism are in good agreement with the results of GRI 3.0.

As the final validation of WD two-step chemical mechanism, the result obtained using “Fluent” CFD software with WD mechanism for concrete simulation of the combustion process in atmospheric premixed burner, showed very good correlations with experimental measurements [4].

ACKNOWLEDGMENT

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NOMENCLATURE

A_i	pre exponential factor
E_i	activation energy
k_{fi}	reaction rate
L_i	length of domain for i-th iteration
m	mass flow rate
p_{sis}	system pressure
T	temperature
T_{end}	predicted outlet temperature
T_{fix}	referent (fixed) point temperature
T_{init}	inlet gas and air temperature

Greek symbols

β_i	temperature coefficient
λ	air ratio coefficient

Acronyms

GRI	Gas Research Institute
WD	C.K. Westbrook & F.L. Dryer mechanism
CFD	Computational Fluid Dynamic

SNL Sandia National Laboratories mechanism
SD San Diego Laboratories mechanism
CPU Central Processor Unit
CARM Computed Assisted Reduction Method

**МОГУЋНОСТИ УПОТРЕБЕ ВЕОМА
РЕДУКОВАНИХ ХЕМИЈСКИХ МЕХАНИЗАМА
У НУМЕРИЧКОМ МОДЕЛИРАЊУ ПРОЦЕСА
САГОРЕВАЊА**

**Мирољуб Ацић, Васко Фотев, Војислав Јовичић,
Александар Миливојевић, Гордана Милекић,
Вук Ацић, Мартина Богнер**

Резултати нумеричких моделирања презентовани у овом раду, део су истраживања лабораторије за сагоревање Машинског факултета у Београду, спроведеног у оквиру FP6 пројекта "FlexHEAT", који су заједно реализовале институције из шест

европских земаља а који је финансиран од стране Европске уније (www.flexheat.uni-erlangen.de).

У раду су презентовани упоредни резултати нумеричких прорачуна којима се симулира сагоревање горива на бази метана, (природни гас, српски гас, биогаз и сл.), а који су добијени коришћењем, експериментално провереног, комплетног хемијског механизма GRI 3.0 који чини 325 хемијских реакција и одговарајућег веома редукованог хемијског механизма, кога чине 2 хемијске реакције (од којих је једна повратна), развијеног на бази двостепеног *C.K. Westbrook & F.L. Dryer* (WD) модела.

Резултати су добијени употребом програмског пакета "ChemKin" и детерминишу област и могућност примене овако значајно редукованих хемијских механизма у CFD прорачунима, у ситуацијама када комплексност самог струјања са хемијским реакцијама кроз сложене геометрије горионика и пећи не дозвољава употребу сложенијих хемијских механизма.