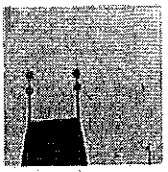
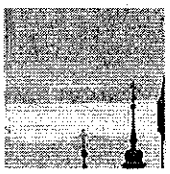
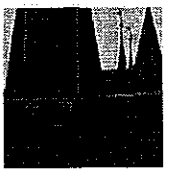
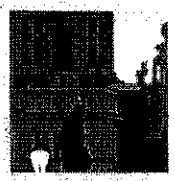
CRU | EVENTS

A DIVISION OF CRU GROUP







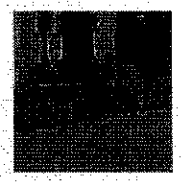


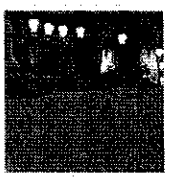
International Conference & Exhibition

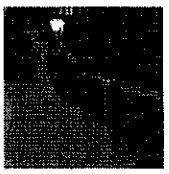
SULPHUR 2010

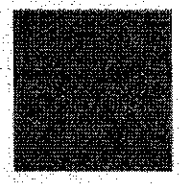
Sulphur | Sulphuric Acid | Sulphur Dioxide

1-4 November 2010, Prague Hilton, Czech Republic









TECHNICAL PREPRINTS

International Conference & Exhibition
SULPHUR 2010
Sulphur | Sulphuric Acid | Sulphur Dioxide
1-4 November 2010, Prague Hilton
Czech Republic

Investigation of the SO_2 Production Process by Combustion of Sulphur-Containing Substances Using Computational Fluid Dynamics

M. HARASEK, C. MAIER

Vienna University of Technology
Institute of Chemical Engineering
Vienna, Austria

H. HABERFELNER

DUMAG Brenner-Technologie Ges. mbH
Traiskirchen, Austria

An extensive CFD model was developed capable of capturing the phenomena occurring during the combustion of sulphur and sulphur-containing substances to produce sulphur dioxide (SO_2). The model includes a comprehensive description of the combustion of liquid sulphur droplets, accounting for the different modes of sulphur molecules during the pyrolysis phase. To represent the conversion of injected sulphuric acid, a proper set of pyrolysis reactions was implemented. Further reaction mechanisms were embedded to model hydrocarbon combustion. By inclusion of turbulence effects as well as radiative heat transfer, a thorough model was designed, allowing for in-depth analysis of the combustion system investigated. This model was successfully applied to practical combustion conditions, providing a convenient tool for the optimisation of existing plants as well as for the scale-up or design of new combustion facilities.

INTRODUCTION

Aiming for further optimisation of the already well-established furnace system developed by DUMAG Brenner-Technologie Ges.mbH, the sulphur combustion process was investigated in detail using Computational Fluid Dynamics (CFD). By operating these types of combustion systems, sulphur dioxide (SO_2) is produced employing a number of sulphur-containing substances. The SO_2 obtained is fed to subsequent process steps to produce sulphuric acid. However, to obtain maximal conversion grades to SO_2, the combustion process has to be designed optimally.

The performance of the furnace systems deployed for sulphur combustion is strongly dependent on the applied set-up, such as:

- furnace geometry;
- configuration of guiding plates;
- injection characteristics of liquid substances; and
- composition of injected gases.

By carrying out CFD analysis, a substantial contribution to better understanding of the processes going on in combustion chambers of such incineration plants can be obtained.

THE COMBUSTION FACILITY

The incinerator examined can be used for the combustion of a wide range of substances. The combustion chamber has a diameter of 3.3 m, the overall length is about 13.7 m (see Fig. 1). The combustion air is injected with superimposed swirling motion – by implementing adjustable guiding blades, the apparent swirl rate can be changed to find optimal operating conditions.

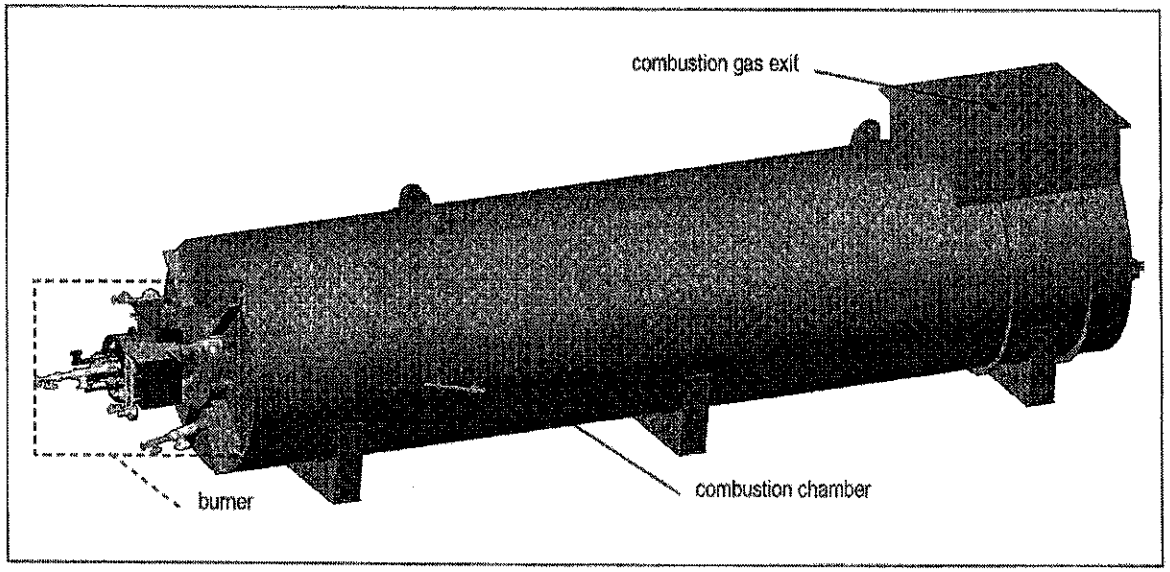


Fig. 1: Furnace – overview

Liquid sulphur is injected in the centre of the burner. By applying the ultrasonic nozzle invented by DUMAG, the complete liquid jet can be atomised into fine droplets. The nozzle is capable of reliable and stable atomisation of liquids with high viscosity. Using this ultra-sonic nozzle, sulphur is atomised through a preheated armature group and burner lance at a temperature of 140°C.

Sulphuric acid rejected from the acid production process is fed to the furnace using jet nozzles. Further waste streams are recycled by injecting off-gases containing H_2S amongst other gaseous constituents. These substances are decomposed thermally and oxidised to form SO_2.

To ensure reliable start-up and shut-down procedures, methane or heating oil can be fed to the combustion chamber. In terms of flexibility – especially if the mixture of sulphur-containing fuel types exhibits low heating values – these hydrocarbons can be fed continuously to support complete sulphur conversion.

The conditions of the operating point investigated in the CFD simulations are summarised in Table 1.

Table 1
Feed Streams to Combustion Chamber

Feed stream		
Liquid sulphur	kg/h	430
Sour gas	Nm³/h	1600
Spent sulphuric acid	kg/h	5880
Combustion air	Nm³/h	9500

SIMULATION MODEL

In this research study, an extensive CFD model was developed to be able to capture all the phenomena occurring during the combustion/conversion of the above mentioned agents.

Models describing the combustion of common fuel types such as oil, methane or even heterogeneous coal combustion are well established and available in commercial CFD codes. However, the same principles are applicable for modelling the combustion of sulphur and sulphur-containing substances as main fuel species [1]. An essential prerequisite for the accurate prediction of the combustion process is proper modelling of the underlying physical and chemical processes by implementing convenient sub-models for combustion, thermophysical properties, etc. [2].

Performing CFD, in the first step the considered geometry has to be implemented and divided spatially in discrete volume elements. In this work, the furnace and burner section is represented by approximately 900,000 hexahedral cells. For each of the discrete elements, balance equations for mass, energy, species, turbulence-specific quantities, etc., are solved iteratively.

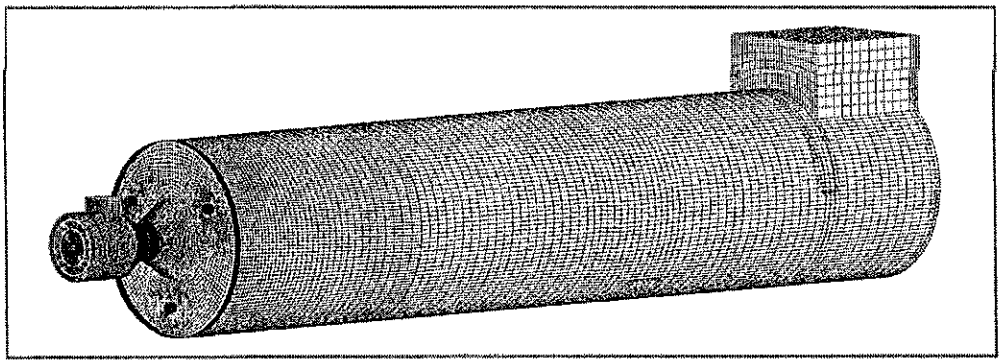


Fig. 2: Computational grid

The simulation work was done using the commercially available multi-purpose software tool FLUENT®, version 6.3.26 [3]. The set-up of the model developed in this study will be presented in the following sections.

Turbulence

In many cases, the flow field in industrial apparatuses exhibits turbulent behaviour. For turbulent flows, usually the Reynolds-averaged Navier-Stokes equations are employed [4]. To perform the calculations, the unknown elements of the Reynolds stress tensor have to be calculated. These closure terms are estimated by turbulence-models. In the present work, the two-equation k-ε model [5] was used.

Liquid injection

During the atomisation process millions of droplets are formed. In the CFD model, these droplets are tracked in a Lagrangian frame of reference. This second phase consists of spherical droplets dispersed in the surrounding continuous gas phase. The trajectories of these discrete particles are calculated as well as heat and mass transfer to or from them [3]. Droplet size distributions were modelled using the widely applied Rosin Rammler function.

In the furnace, sulphur is present in its various polymeric forms. Up to about 160°C, the liquid sulphur mainly consists of S_8 polymers. With increasing temperature, the sulphur molecules change to S_6 and S_4 in different proportions (Fig. 3). Accordingly, thermophysical properties such as viscosity, density and specific heat also change. When the boiling point (445°C) is reached, volatile sulphur is released. In the gas phase, endothermic decomposition of the polymers takes place – at higher temperatures (above 1,000°C), the sulphur vapour appears practically exclusively as S_2.

Radiation model

The heat transfer due to radiation was accounted for by the discrete ordinates (DO) model. This model solves the radiative heat flux for a discrete number of spatial directions. It is applicable to a wide range of optical thickness and is appropriate for the simulation of industrial furnaces [7].

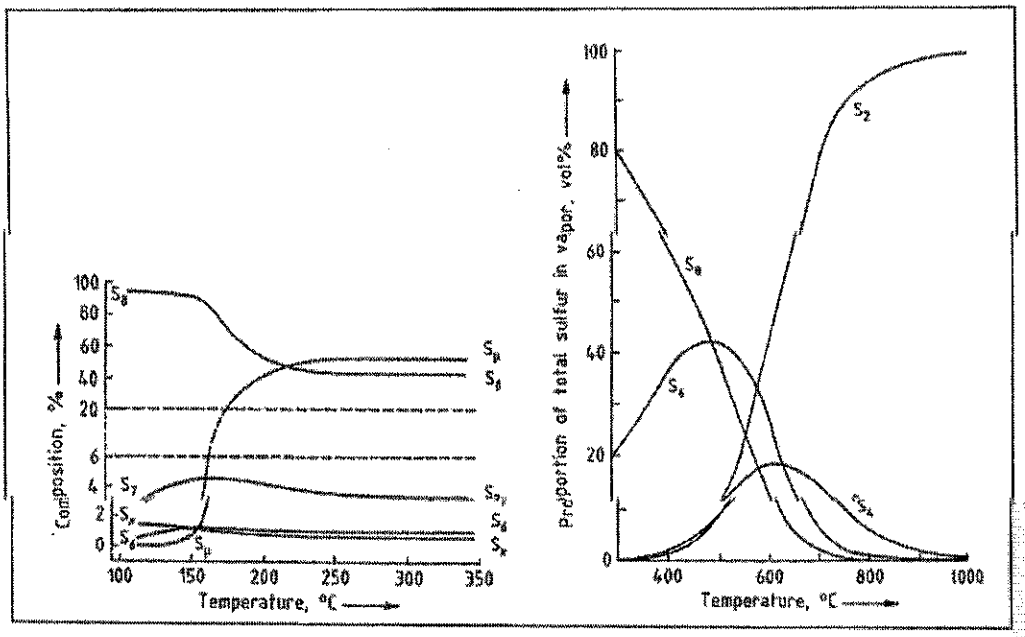


Fig. 3: Composition of liquid and gaseous sulphur [6]

The interaction between gases and the radiation is modelled using the "weighted sum of gray gases" approach. This set up accounts for local changes in the gas composition and therefore represents a more accurate description of the absorption coefficients than the simpler grey gas model [8]. The model was improved by the implementation of user-defined sub-routines (see also [9-10]). In this work, apart from CO_2 and H_2O, the absorption characteristics of SO_2 are considered.

Combustion model

The Eddy Dissipation Model [11] was used to describe the combustion process in the gas phase. The chemical kinetics were implemented by introducing a number of Arrhenius-type reactions. In the model, ten species were used to describe the chemical composition in the gas phase: S_2, H_2S, H_2SO_4, C_8H_{18}, O_2, H_2O, CO_2, SO_2, SO_3 and N_2.

As oxidation kinetics of H_2S and S_2 are typically fast at the temperatures present in combustion furnaces, this step was modelled to be mixture-controlled [1]:

$$H_2S + 1.5O_2 \xrightarrow{k_{mix}} SO_2 + H_2O$$

$$S_2 + 2O_2 \xrightarrow{k_{mix}} 2SO_2$$

The dissociation of injected sulphuric acid was modelled to take place in the gas phase. For this step, the kinetic rate was computed from the reversed reaction rate (reaction data from [12]) using the concept of standard state enthalpies and entropies.

$$H_2SO_4 \xrightarrow{k_{H_2SO_4}} SO_3 + H_2O \qquad k_{H_2SO_4} = 3.842 \cdot 10^{14} \cdot T^{-1} \cdot e^{\frac{9.5105 \cdot 10^7}{8314 \cdot T}}$$

Sulphur trioxide, SO_3, is further thermally decomposed to the desired product gas SO_2. This step is kinetically limited and mainly takes place via [13]:

$$SO_3(+M) \leftrightarrow SO_2 + O(+M)$$

$$SO_3 + O \leftrightarrow SO_2 + O_2$$

The analysis of these reactions using a detailed reaction mechanism in combination with steady-state analysis for the O radical and further analysis of reversibilities yields the following kinetic expression for SO_3 dissociation [13]:

$$SO_3 \xrightarrow{k_{SO_3}} SO_2 + \tfrac{1}{2}O_2 \qquad k_{SO_3} = 11.4 \cdot 10^{17} \cdot e^{\frac{3.3256 \cdot 10^8}{R \cdot T}}$$

During the start-up phase of the incinerator, oil is injected to provide for the power necessary to heat up the equipment to the operating conditions. An overall combustion reaction was implemented to account for the oxidation of the oil species:

$$C_8H_{18} + 12.5O_2 \xrightarrow{k_{C_8H_{18}}} 8CO_2 + 9H_2O$$

SIMULATION RESULTS

Examining the data field calculated by the CFD solver, different aspects concerning the flow-, temperature- and concentration field can be evaluated. Figure 4 shows the evolution of the velocity magnitude on a vertical cutting plane through the furnace. The highest velocities are found in the flame zone near the centre of the combustion chamber. Owing to these relatively high velocities in the centre, stable vortices are formed providing for internal recirculation of combustion products (Fig. 5). Using the CFD model, different geometric conditions, e.g. effects of swirl, guiding plates or *mixing characteristics, can be investigated.*

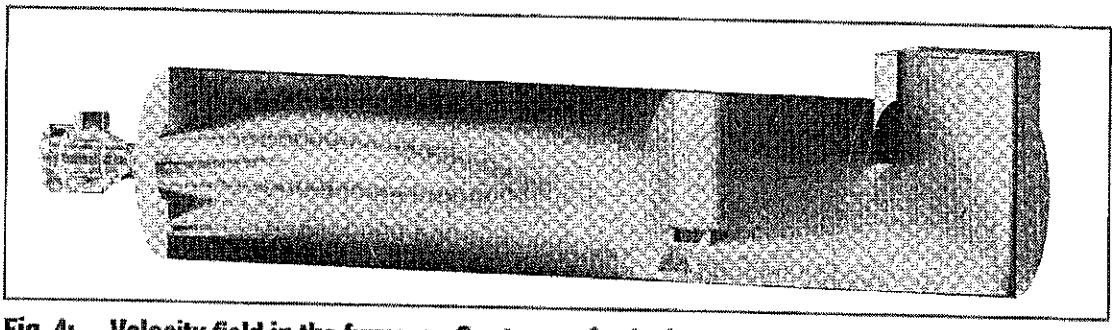


Fig. 4: Velocity field in the furnace. Contours of velocity magnitude

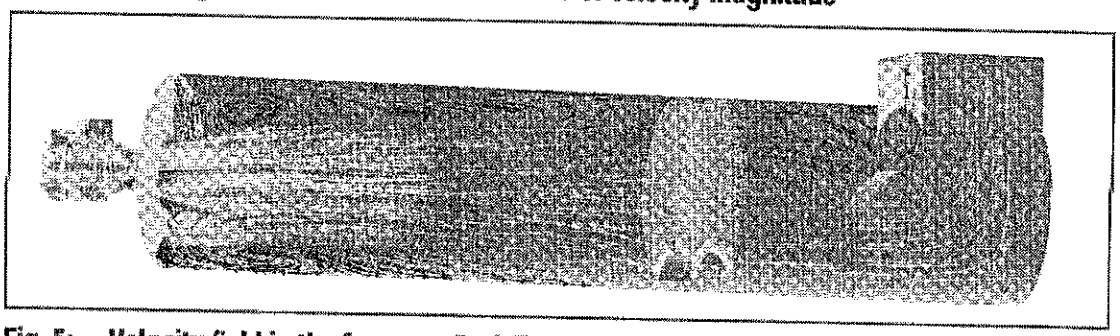


Fig. 5: Velocity field in the furnace. Path lines

A sketch of the temperature field in the gas phase is shown in Fig. 6. In combination with concentration fields (e. g. oxygen concentration), even the prediction of NOx formation tendencies is possible.

Droplet trajectories (see Fig. 7) were evaluated to get data for burn-out times for the injected liquids. Furthermore, the influence of droplet size distributions on the evaporation rates can be studied.

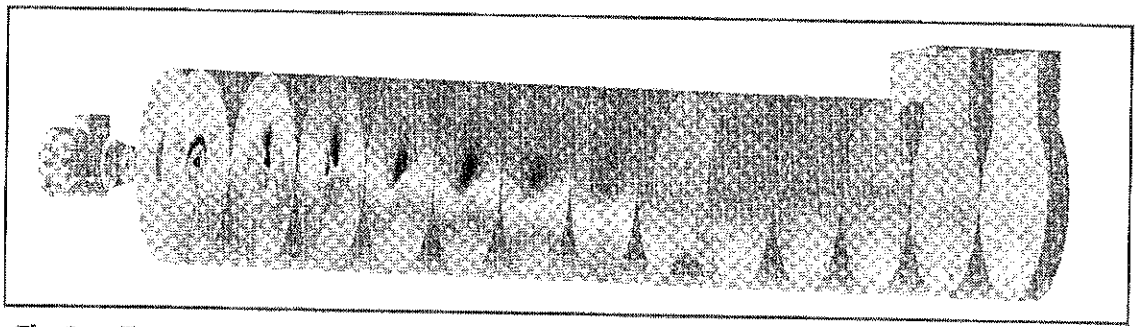


Fig. 6: Temperature contours

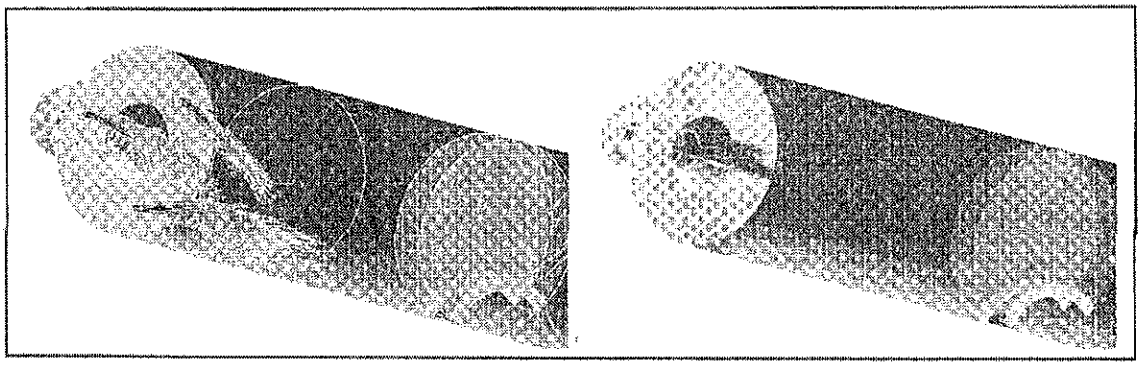


Fig. 7: Particle tracks for injected droplets, coloured by droplet temperature.
Left sketch: Sulphuric acid, Right: Liquid sulphur

Sulphur trioxide (Fig. 8) in the furnace chamber originates from the dissociation of injected spent acid. Due to high temperatures and retention times available in the furnace, the SO_3 is almost completely converted to SO_2 (see Fig. 9).

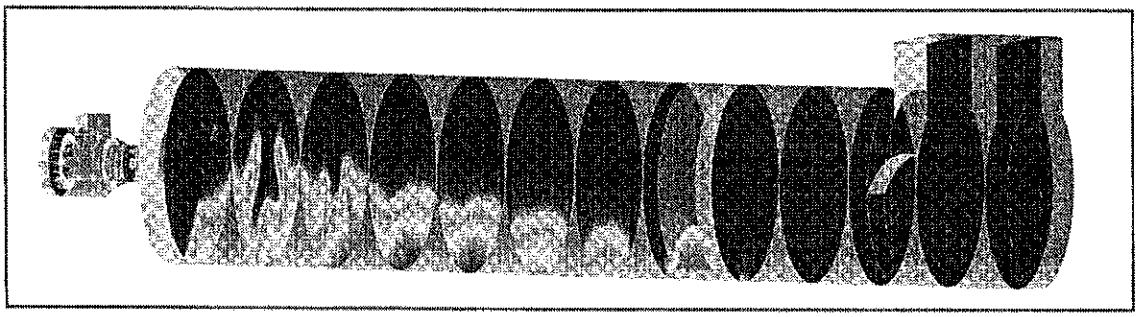


Fig. 8: SO_3 contours

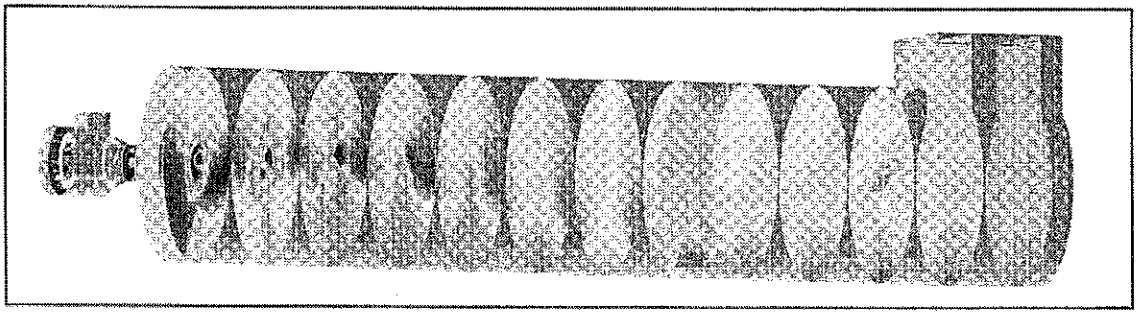


Fig. 9: SO_2 contours

SUMMARY

Computational Fluid Dynamics provide a promising tool that can deliver insight into combustion processes in a time- and cost-effective way, thus featuring a substantial contribution to the understanding of such devices. By implementing an in-depth description of the reactor geometry in combination with proper models describing the physical processes, operating conditions and geometric boundaries can be improved in order to obtain optimal parameters.

In this work, the conditions in incineration systems for combustion of sulphur containing substances were studied. The developed model was successfully applied for the investigation of different geometric configurations and fuel injection conditions.

References

1. Brereton, C., et al.: "Studies of the combustion process in a sulphur furnace through computational fluid dynamics". **Sulphur 2009**, Vancouver (Nov 2009). Preprints, pp. 63-67.

2. Maier, C., et al.: "Improvement of small-scale log wood stoves by experimental investigation combined with Computational Fluid Dynamics". **SPEIC10:Towards Sustainable Combustion**, Tenerife (Jun 2010).
3. Fluent, http://www.fluent.com., FLUENT, Inc. (2007) (Hrsg.).
4. Menter, F. R.: "Two-equation eddy-viscosity turbulence models for engineering applications". *AIAAJ.* **32** (8), 1598-1605 (1994).
5. Shih, T.-H., et al.: "A new k-ε eddy-viscosity model for high Reynolds Number turbulent flows – Model development and validation". *Computers & Fluids*, **24** (3), 227-238 (1995).
6. Nehb, W.; Vydra, K.: "Sulfur". In "Ullmann's Encyclopedia of Industrial Chemistry", ed. M. Bohnet et al., p. 68. Wiley-VCH (2009).
7. Mueller, C.; Brink, A.; Hupa M.: "Numerical simulation of the combustion behavior of different biomasses in a bubbling fluidized bed boiler". **18th International Conference on Fluidized Bed Combustion 2005**. ASME. Proceedings, pp. 771-781.
8. Christo, F. C.; Dally B. B.: "Modeling turbulent reacting jets issuing into a hot and diluted coflow". *Combustion and Flame* **142** (1), 117-129 (2005).
9. Harasek, M., et al.: "Evaluation of the high-temperature conversion of plastic particles after injection into blast furnace raceway using CFD simulations". AIChE Annual Meeting, Salt Lake City (2007).
10. Maier, C.; Jordan, C.; Harasek M.: "Numerical simulation of the post combustion zone of biomass firing systems". **European Combustion Meeting 2009**, Vienna (Apr 2009).
11. Magnussen, B. F.; Hjertager, B. H.: "On mathematical models of turbulent combustion with special emphasis on soot formation and combustion". *Symposium (International) on Combustion*. **16** (1), 719-729 (1977).
12. Hughes, J., et al.: "Experimental and modelling study of sulfur- and nitrogen-doped premixed methane flames at low pressure". *Faraday Discuss.* **119**, 337-352 (2001).
13. Yilmaz, A., et al.: "Thermal dissociation of SO_3 at 1000-1400K". *J. Phys. Chem. A.* **110** (21), 6654-6659 (2006).