NUMERICAL STUDY ON HOMOGENEOUS SO₂ OXIDATION IN HIGH TEMPERATURE CONDITIONS

Significant content of SO₃ in exhaust gases generates difficulties in maintenance of metallurgical plants and large combustion installations. To minimize the range of this problem, numerical models of reacting flow can be introduced to the designed process. Modeling combustion and post combustion of SO₂ formation requires adding reaction mechanism of reactive mixture to flow equations. In this work three kinetic mechanisms of SO₂ oxidation have been used to predict SO₃ formation, expressed in SO₃ outlet concentration and SO₂ to SO₃ conversion rate. Physical model of flow through quartz glass tube, based on [Belo et al. 2014] experiment, has been created and implemented in Ansys Fluent. Difference between experimental data and model calculations results have been presented as a function of species concentration and temperature.

Key words: SO₂, SO₃, oxidation, CFD, Fluent, kinetic mechanism

1. INTRODUCTION

According to the newest European pollutant regulations, restricted limits of sulfur oxides emission must be achieved [EIPPCB 2010]. Sulfur oxides, as an exhaust gases component, are released to atmosphere. It leads directly to acid aerosols formation and degradation of natural environment. Acidic oxide, like SO₂, in presence of water may produce lean acid vapor, but only SO₃ instantly reacts to highly corrosive sulfuric acid, H₂SO₄. Process of SO₂ oxidation can be mainly divided into two paths:

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– homogeneous oxidation, determined by thermodynamical process parameters and species fractions;
– heterogeneous oxidation, forced by catalytic impact of vanadium or iron oxides on activation energy.

In this article will be presented influence of thermal and flow parameters on amount of formed SO₃ in outlet, in various temperature and configuration of species fraction. This approach refers to heat and power combustion system in industrial applications, where homogeneous oxidation takes main part. The impact of fly ash on oxidation is excluded due to its catalytic properties and heterogeneous character.

Predicting pollutant amount during design step would give an opportunity to optimize combustion chamber construction and flow system parameters. It is essential to prepare whole installation for sulfur oxides emission limitation. In existing conventional large combustion plants this goal can be obtained by using low-sulfur fuel or investment in large desulphurization units. Low concentration of SOx in exhaust gases appears as first, but not only single point in pollutant regulations fulfillment. Amount of SO₃ above 10 ppmv can make serious problem, visible in blue plume at the stack. Overall quantity of SO₃ on outlet may vary, difference between formed and emitted sulfur trioxide depends on H₂SO condensation, which takes place below dew point parameters. Sulfuric acid on installation surfaces causes corrosion and lowers expected gas analyzers indications in outlet.

Oil refinery and metallurgical processes on copper, lead and zinc ores also produce large amount of waste gas, rich in sulfur oxides. Lean H₂SO₄ vapor lowers value of condensed acid gas, extracted from exhaust gas stream, which is driven to the catalytic reactors beds in the acid plants. Catalytic effect of vanadium and iron oxides lowers activation energy of SO₂ oxidation and shifts reaction to energetically efficient region of temperatures (below 400 ºC). Fly ashes, due to their composition, force unwanted oxidation in range 500–700 ºC. Homogeneous reaction takes place mainly in higher temperatures and becomes significant above 900 ºC. In this paper, next to temperature, influence of O₂, H₂O, SO₂ inlet concentration on SO₃ formation in outlet have been investigated.

Summarizing, the significant content of SO₃ in exhaust gases generates difficulties in oil refinery and metallurgy. To minimize range of sulfur pollution problem, numerical models of reacting flow can be introduced to the design process. Modeling post-combustion SO₃ formation requires addition of reaction mechanism to the flow equations. In this work three kinetic mechanisms of SO₂ oxidation have been used to predict SO₃ formation, expressed in SO₃ outlet concentration and SO₂ to SO₃ conversion rate. Physical model of flow through quartz glass tube, based on [Belo et al. 2014] experiment, have been created and implemented in Ansys Fluent. Difference between experimental data and model calculations results are presented in function of species concentration and temperature.
2. NUMERICAL INVESTIGATION

2.1. Model setup

Numerical model, used in this study, represents an electrically heated quartz tube flow reactor, being a part of experimental setup from [Belo et al. 2014] work. Presented model illustrates $\frac{1}{4}$ of tube geometry, with inner diameter 12 mm and length 250 mm, bound with symmetry constrains. Mesh consists of 85 000 hexagon elements, with average element quality 0,935, built on sweepable surface.

Next to symmetry boundary condition and pressure-outlet, velocity-inlet value was calculated on 0,0872 m/s at 353 K and 1 atm, from combined flow rate 0,5 L/min at 298 K and 1 atm. In the most of cases, physically the flow is laminar due to the slow motion of fluid and low Re number. However, the combustion model used with kinetic mechanisms requires enabled turbulence. Turbulence is presented by solving RSM equations with standard coefficients, which introduce dissipative vortex. Base temperature and mole species fractions were specified on 1173 K, 0,1% SO$_2$, 5% vol O$_2$, 3% vol H$_2$O and balance N$_2$. Temperature variation depends on the modification of thermal condition of fixed wall temperature and enabling of radiation equation (DO model).

The kinetic mechanisms, including SO$_2$ reactions, are the main point of this work calculation. Species transport with EDC includes reactions, which rate is expressed with Arrhenius equation coefficients. Products formation limitation is achieved by both, mixing laws as impact of activation energy $E_a$ and pre-exponential factor $A$. In this work, three kinetic reactions mechanisms for H$_2$O/O$_2$/SO$_2$ system have been chosen: Karmlich and Hunter [Karmlich 1980, Hunter 1982], Alzuetas [Alzuetas et al. 2001] and Mueller [Mueller et al. 2000]. Reduced mechanism from Karmlich [Karmlich 1980] consist of 15 species with radicals, 8 reversible reactions for SO$_3$, 2 for SO$_2$ and it is commonly used in Fluent’s SO$_x$ module. In theory, it closely follows SO$_2$ concentration. However, the correlation between SO and SH is not kept. SO$_3$ equations are added from Hunter [Hunter 1982] work:

$$SO_2 + O + M \rightleftharpoons SO_3 + M \quad (1)$$
$$SO_2 + O_2 \rightleftharpoons SO_3 + O \quad (2)$$

Two reversible reactions above are principle mechanisms for SO$_3$ formation in flame zone. However, in post-combustion conditions oxidation of SO$_2$ by O$_2$ is negligible. In addition, even high concentration of O atoms is not sufficient to provide SO$_3$ formation. To check correctness of these rules, mechanism has been used as direct implementation into Fluent.
Secondly, reduced mechanism consists of 15 species and 9 reversible key reactions, extracted from full mechanism in Srivastava [Srivastava et al. 2004] with original Alzueta [Alzueta et al. 2001] coefficients, has been considered. Mechanism introduces the consumption of SO$_3$ by hydroxy sulfonyl radicals in the equations. The HOSO and HOSO$_2$ are middle steps species in SO$_2$ oxidation, initiated by OH:

\[
\begin{align*}
SO_2 + OH + M & \rightleftharpoons HOSO_2 + M \\
HOSO_2 + O_2 & \rightleftharpoons SO_3 + HO_2
\end{align*}
\] (3) (4)

According to Salonen [Salonen et al. 2007], in the presence of OH radicals and water vapor SO$_2$ nucleates better than sulfuric acid taken from the liquid phase. The HOSO radicals are formed in high temperature zones. It results in amount of acid vapor above dew point temperatures.

\[
SO_2 + H_2O + M \rightleftharpoons H_2SO_4 + M
\] (5)

The formation of sulfuric acid is not included in described mechanisms. The water absorbs SO$_3$, but amount of SO$_3$ consumed by this reaction affects SO$_3$ volume flow rate in outlet and correctness of calculation of SO$_2$/SO$_3$ conversion factor.

Thirdly, full mechanism, developed by Mueller [Mueller et al. 2000], presents multistep H$_2$O/O$_2$/SO$_2$ system, with optional CO and NO sub-mechanisms including their mutual interactions. It is built by 50 species and 180 reactions, which implementation doubled required long computation time. In all cases, CO$_2$ and H$_2$O species are present due to the calculation of absorption coefficient for the radiation model.

### 2.2. Results

Detailed chemical data for each work point was obtained by changing inlet species mole fraction, under relaxation factors and clearing ISAT table. This approach may cause slight over prediction of parameters on first point of each run in comparison to the next calculation points. It is effect of longer calculations on starting boundary conditions without table clearing.

The mole SO$_3$ fraction in the function of flow parameters, given in ppmv, is the most important result quantity of this work. The SO$_3$ content, representing amount of oxidized SO$_2$, divided by inlet SO$_2$ mole fraction, gives SO$_2$/SO$_3$ conversion factor, as given below:
Presented graphs of SO$_3$ output and conversion factor may have different trajectory only in case of rising SO$_2$ inlet concentration. In other issues SO$_3$ outlet fraction graph corresponds only straightly to SO$_2$/SO$_3$ data series and can be neglected.

Chosen kinetic reaction mechanisms solution has been compared to results from [Belo et al. 2014] work. Geometry of the quartz tube reactor and input parameters for calculation points fit in test rig conditions. Results of numerical investigation of SO$_2$ oxidation in function of temperature and species fraction variation are shown at Fig. 1.

Fig. 1. Calculated SO$_3$ mole fraction on outlet and conversion factor for SO$_2$ oxidation, variable SO$_2$, 1173 K, 5% vol O$_2$, 3% vol H$_2$O, balance N$_2$

Increase of SO$_2$ mole fraction in inlet should result in SO$_3$ outlet concentration increase. From presented mechanisms only one results in non-zero fractions detailed multistep Mueller system. However, overall amount of oxidized SO$_2$ is mostly ten times over predicted, in comparison to laboratory tests, with even higher starting point. In large combustion plants, conversion factor is estimated on values
up to 1%. On this base only points for 2000–2500 ppm are considered as acceptable. Karmlich and Azuleta mechanisms give response in SO$_3$ concentration at level lower than ppb (1e-09). Additionally, cases with Karmlich mechanism calculations proceed without any remarkable reactions undergoing. Alzueta kinetic system can provide formation of SO and SH, characteristic radicals bound to SO$_2$ decomposition and H$_2$S combustion. Issue, where SO$_2$ is only source of sulfur in flow and SO, SH are present in outlet gases, needs to be redesign in reaction mechanism. In other cases problems with short mechanisms, without any significant undergoing oxidation reactions are also clearly visible at Fig. 2 and Fig. 3.

Fig. 2. Conversion factor for SO$_2$ oxidation, 1000 ppm vol. SO$_2$, variable O$_2$ and H$_2$O, balance N$_2$. 
Numerical Study on Homogeneous SO₂ Oxidation in High Temperature Conditions

Fig. 3. Conversion factor for SO₂ oxidation, 1000 ppm vol. SO₂, variable T, balance N₂

Figure above shows that detailed SO₂ oxidation mechanism is sensitive to high temperature conditions. Main oxidation process is defined with high activation energy, what is convergent with experimental results, but real process turns to be slower than reactions undergoing in modelled flow.

3. CONCLUSIONS

Modeling of SO₂ oxidation with reduced and short mechanisms, including only two reactions involving SO₃, is incorrect approach. Detailed multistep mechanism takes more computational time. However it gives non-zero results, which are worth of consideration. Over prediction of concentration can be reduced with changing initialization and calculation method or modifying factors connected to Arrhenius equation. Results obtained in the end of each run were only 2–3 times higher than Belo test outcome, what gives information about positive effect of clearing ISAT table and increasing number of iteration after solution stabilization. Fluent may be efficient tool for complex cases. However this kind of work could be also done in 1D Cantera or Chemkin solver, without any difficulties connected to initialization and iteration number. Modeling exhaust gases behavior without including essential combustion products, like CO₂, in the composition is also generating discrepancies between test cases and real combustion conditions. The main problem of the studied case is very low concentration of oxidized SO₂ in comparison to SO₂ amount in inlet. Even using advanced chemical correlations may be not enough to precise prediction of conversion factor, when target concentration is on level of 2–3 ppmv.
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ANALIZA NUMERYCZNA PROCESU HOMOGENICZNEGO UTLENIANIA SO2 W WARUNKACH WYSOKICH TEMPERATUR

Streszczenie

Znacząca zawartość SO3 w spalinach powoduje trudności w użytkowaniu instalacji metalurgicznych oraz energetycznym spaleniu. W celu minimalizacji zasięgu tego problemu, do etapu projektowania instalacji mogą zostać wprowadzone modele reakcji chemicznych przepływającego płynu. Modelowanie powstawania SO3 w trakcie procesu spalania oraz w elementach instalacji spalinowej wymaga uzupełnienia równań przepływu o mechanizmy reagującej mieszanki. W tej pracy zostały wykorzystane trzy mechanizmy uwzględniające...
utlenianie SO₂ do predykcji formacji SO₃, wyrażonej przez koncentrację wylotową SO₃ i współczynnik konwersji SO₂ do SO₃. Model fizyczny przepływu przez szklaną rurę, bazujący na eksperymencie [Belo et al. 2014], został przygotowany i zaimplementowany do oprogramowania Ansys Fluent. Różnice pomiędzy danymi eksperymentalnymi oraz obliczeniami dla poszczególnych modeli zostały zaprezentowane w funkcji koncentracji związków oraz temperatur.

Słowa kluczowe: SO₂, SO₃, utlenianie, CFD, Fluent, mechanizmy kinetyki reakcji
