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NUMERICAL STUDY ON HOMOGENEOUS SO_2 OXIDATION IN HIGH TEMPERATURE CONDITIONS

Significant content of SO_3 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 SO_3 formation requires adding reaction mechanism of reactive mixture to flow equations. In this work three kinetic mechanisms of SO_2 oxidation have been used to predict SO_3 formation, expressed in SO_3 outlet concentration and SO_2 to SO_3 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: SO_2, SO_3, 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 SO_2, in presence of water may produce lean acid vapor, but only SO_3 instantly reacts to highly corrosive sulfuric acid, H_2SO_4. Process of SO_2 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 SO_3 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 SO_3 above 10 ppmv can make serious problem, visible in blue plume at the stack. Overall quantity of SO_3 on outlet may vary, difference between formed and emitted sulfur trioxide depends on H_2SO 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 H_2SO_4 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 SO_2 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 O_2, H_2O, SO_2 inlet concentration on SO_3 formation in outlet have been investigated.

Summarizing, the significant content of SO_3 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 SO_3 formation requires addition of reaction mechanism to the flow equations. In this work three kinetic mechanisms of SO_2 oxidation have been used to predict SO_3 formation, expressed in SO_3 outlet concentration and SO_2 to SO_3 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 ¼ 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_2O 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_3 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 well as impact of activation energy E_a and pre-exponential factor A. In this work, three kinetic reactions mechanisms for $H_2O/O_2/SO_2$ system have been chosen: Karmlich and Hunter [Karmlich 1980, Hunter 1982], Alzueta [Alzueta 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_2, 2 for SO_3 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:

$$SO_2 + O + M \Leftrightarrow SO_3 + M \quad (1)$$

$$SO_2 + O_2 \Leftrightarrow SO_3 + O \quad (2)$$

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 consist 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:

$$SO_2 + OH + M \Leftrightarrow HOSO_2 + M \tag{3}$$

$$HOSO_2 + O_2 \Leftrightarrow SO_3 + HO_2 \tag{4}$$

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.

$$SO_3 + H_2O + M \Leftrightarrow H_2SO_4 + M \tag{5}$$

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 $H_2O/O_2/SO_2$ 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_2O 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:

$$SO_2 / SO_3 = \frac{outlet\ SO_3\ mole\ fraction}{inlet\ SO_2\ mole\ fraction} \times 100\% \quad (6)$$

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.

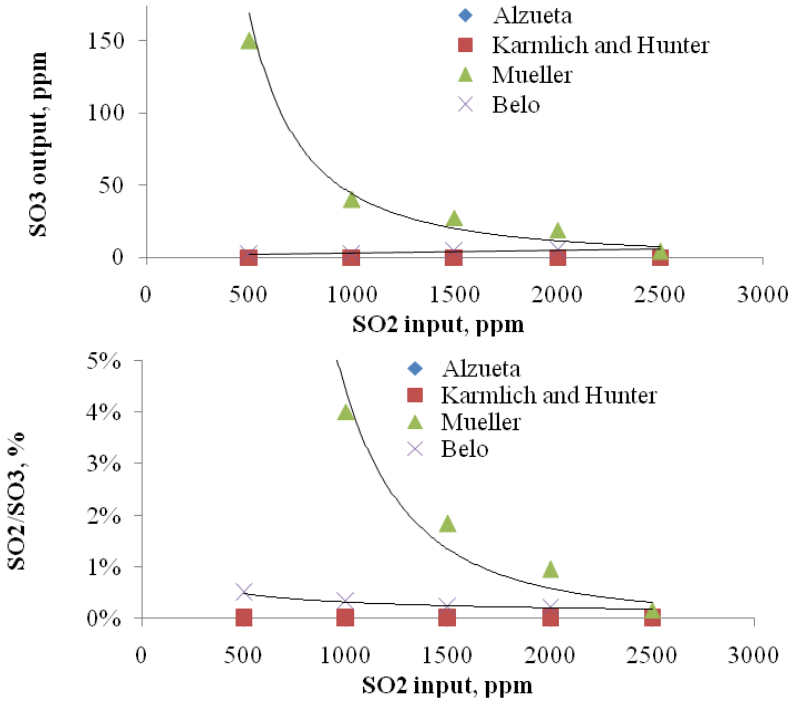

Fig. 1. Calculated SO_3 mole fraction on outlet and conversion factor for SO_2 oxidation, variable SO_2, 1173 K, 5% vol O_2, 3 % vol H_2O, balance N_2

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_2S 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.

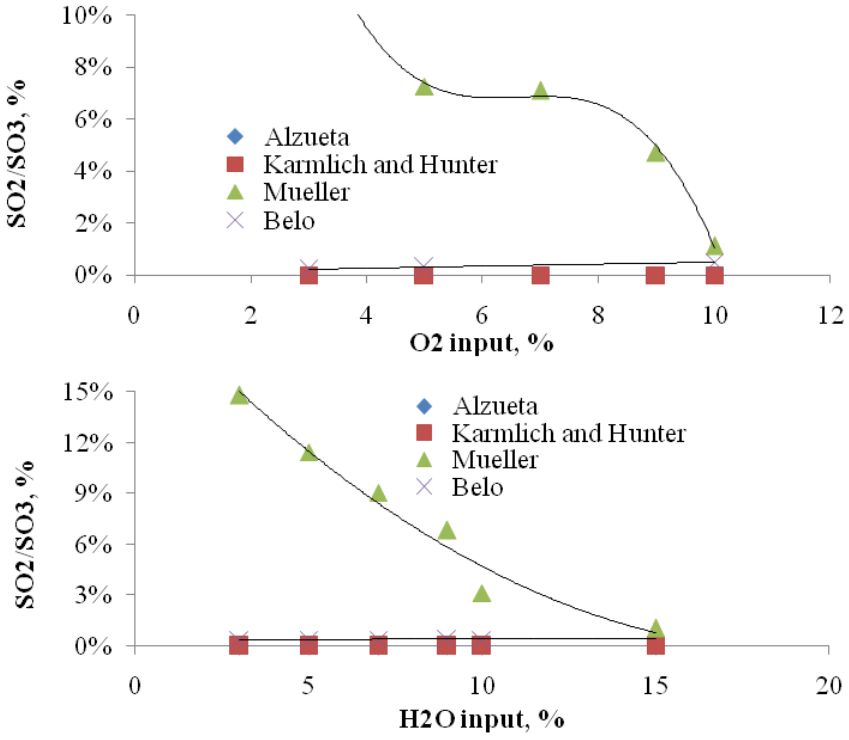

Fig. 2. Conversion factor for SO_2 oxidation, 1000 ppm vol. SO_2 , variable O_2 and H_2O, balance N_2

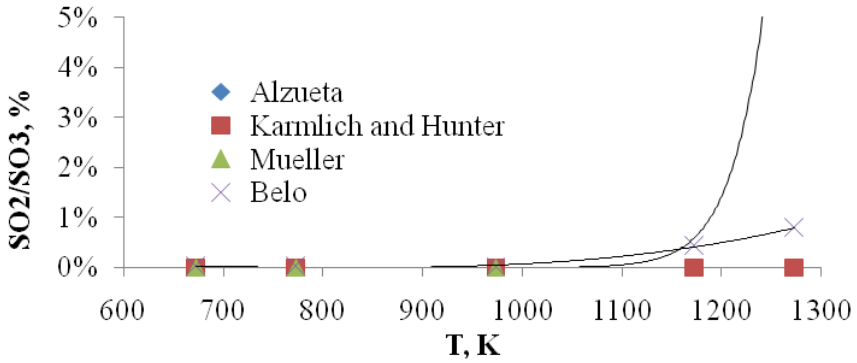

Fig. 3. Conversion factor for SO_2 oxidation, 1000 ppm vol. SO_2 , variable T, balance N_2

Figure above shows that detailed SO_3 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 SO_2 oxidation with reduced and short mechanisms, including only two reactions involving SO_3, 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 CO_2, 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 SO_2 in comparison to SO_2 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 SO_2 W WARUNKACH WYSOKICH TEMPERATUR

Streszczenie

Znacząca zawartość SO_3 w spalinach powoduje trudności w użytkowaniu instalacji metalurgicznych oraz energetycznego spalania. W celu minimalizacji zasięgu tego problemu, do etapu projektowania instalacji mogą zostać wprowadzone modele reakcji chemicznych przepływającego płynu. Modelowanie powstawania SO_3 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 SO_2 do predykcji formacji SO_3, wyrażonej przez koncentrację wylotową SO_3 i współczynnik konwersji SO_2 do SO_3. 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: SO_2, SO_3, utlenianie, CFD, Fluent, mechanizmy kinetyki reakcji