INVESTIGATION OF S₂ + AIR COMBUSTION

N. Sebbar*, T. Zirwes**, P. Habisreutheher*, H. Bockhorn*, D. Trimis*

nadia.sebbar@kit.edu

*Karlsruhe Institute of Technology (KIT), Engler-Bunte-Institute, Combustion Technology, Engler-Bunte Ring 7, D-76131 Karlsruhe, Germany
**Karlsruhe Institute of Technology (KIT), Steinbuch Center for Computing, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

Abstract

This study comprises burning velocity calculations for the combustion of S₂ with air for a wide range of air/fuel ratios. The reaction mechanism used in the flame simulations considers S/N/O reactions. Sensitivity analysis of the computed results is performed to evaluate crucial reaction steps. The results show high sensitivity of the burning velocity to the rate coefficient of the reaction S + O₂ → SO + O. Flame simulations have been performed on the basis of different rate constants for this reaction. Using rate coefficients from literature the calculations exhibit a unusual high burning velocity in the order of 350 cm s⁻¹ at T₀ = 373 K and no influence of the nitrogen-sulphur reactions on the flame behavior.

Introduction

Sulphur on one hand is used on a megaton scale in industrial production process of sulphuric acid. On the other hand, heat generated from sulphur combustion may be used for generation of electricity in closed cycles where, e.g. solar heat is applied to recover elemental sulphur from the combustion products [1]. Experimental and numerical studies on combustion of sulphur combined with hydrogen and hydrocarbons have been performed and detailed C/H/O/S reaction mechanisms are reported in the literature [2, 3, 4, 5, 6]. Still, relatively little research on the combustion and behaviour of pure sulphur are available in the literature.

In the present study burning velocity calculations for the combustion of S₂ with air for a wide range of air/fuel ratios are performed. The simulations use mechanism comprising 27 reactions between the species of the S/N/O-system. The nitrogen reactions are taken from [7, 8] and the GRI [9] mechanism. The impact of the different rate coefficients on laminar burning velocities were analyzed and compared. Different rate parameters from literature and re-estimated values for the determinant reaction S + O₂ → SO + O are used. The effect of N₂ and O₂ on the combustion of sulphur is examined, as well as that of temperature and pressure.

Results and Discussion

1. Mechanism

In a previous study [8], a reaction mechanism involving only sulphur and oxygen species was developed. This mechanism, encompassing 11 reactions, is extracted
from a detailed combustion mechanism developed in [7]. In the present work, reactions involving nitrogen and sulphur reactions are added. The N/S/O-reactions are taken from the original mechanism in [7] and completed with N/O reactions from the GRI-mechanism [9]. The N/S/O reaction mechanism encompassing 27-reactions is listed in Table 1.

2. Laminar burning velocities

Laminar burning velocities $S_L$ have been calculated as a function of the air/fuel ratio $\lambda$. Figure 1 (left) illustrates results at normal pressure ($P = 1$ atm) for two temperatures of the incoming mixture $T_0 = 373$ and $T_0 = 423$ K and the effect of
pressure at $T_0 = 373$ K (right). The air/$S_2$ ratio has been varied in the range $0.2 < \lambda < 3.0$. The air/fuel ratio is based on the stoichiometry of reaction $S_2 + 2O_2 \leftrightarrow 2SO_2$ and the mechanism listed in Table 1 has been used.

![Figure 1](image.png)

**Figure 1.** Laminar burning velocity for $S_2$/air calculated at two temperatures, $T_0 = 373$ K and $T_0 = 423$ K (left) and at two pressures $P = 1$ atm and 5 atm (right).

The calculations show that the highest burning velocity for the combustion of $S_2$ is obtained under slightly rich conditions. As expected from $0.2 < \lambda < 1.0$ (rich region) the flame speed increases to attain a maximum near $300$ cm s$^{-1}$ at $\lambda = 0.85$ and $T_0 = 373$ K and then decreases. The burning velocity profile obtained at higher temperature, namely $T_0 = 423$ K, is significantly above the $T_0 = 373$ K curve and its maximum reaches about $360$ cm s$^{-1}$ at $\lambda = 0.90$. The results show the expected decrease of the laminar burning velocity with pressure.

The results exhibit unusual high burning velocities values, which are unfortunately difficult to confirm since no experimental data are available. In [10] values for $S_L$ for combustion of $H_2S$ are reported which are lower by about a factor of 1/10.

3. **Sensitivity analysis**

In order to identify the reactions having most impact on the burning velocity and to characterize the effect of nitrogen species in the S/N/O-system, sensitivity analysis was performed at stoichiometric air/fuel ratio, $\lambda = 1.0$. The sensitivity coefficients reflect a relative change of the model response, caused by a relative change of the rate coefficient of a specific reaction.

Figure 2 demonstrates that reaction $S + O_2 \rightarrow SO + O$ is one of the determinant steps in the oxidation of $S_2$. At 1 atm and $T_0 = 373$ K all other reactions exhibit a significant lower impact on $S_L$ at stoichiometric mixture composition. Figure 2 reveals also that none of the reactions involving nitrogen (reactions 12 to 27) has even a small impact on the flame velocity. New reactions involving the interaction of nitrogen species with sulphur and oxygen species are being developed and will be reported in a near future.
Figure 2: Sensitivity coefficients with respect to the burning velocity at stoichiometric conditions ($\lambda = 1$), $T_0 = 373$ K and $P = 1$ atm.

4. Rate coefficients from literature

Since reaction (1) turned out to be the crucial and determinant step for the combustion of $S_2$ with air, the rate coefficient of this reaction was re-evaluated with quantum chemistry methods [8] and has been employed in the numerical simulations. The results are compared with simulations including different rate coefficient reported in the literature [7, 11, 3]. The rate parameters of reaction (1) as well as are those reported in the literature are listed in Table 2 along with the corresponding references.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k = A T^b \exp(-T_A/T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S + O_2 \rightarrow SO + O$ [7] basic mechanism</td>
<td>$5.20E+06$ 1.8 -600.0</td>
</tr>
<tr>
<td>$S + O_2 \rightarrow SO + O$ [11] Titova</td>
<td>$6.32E+11$ 0.5 0.0</td>
</tr>
<tr>
<td>$S + O_2 \rightarrow SO + O$ [3] Glarborg</td>
<td>$5.40E+05$ 2.11 -729.7</td>
</tr>
<tr>
<td>$S + O_2 \rightarrow SO + O$ singlet [8]</td>
<td>$2.69E+10$ 0.15 5358.8</td>
</tr>
<tr>
<td>$S + O_2 \rightarrow SO + O$ triplet [8]</td>
<td>$1.09E+11$ 0.15 2369.4</td>
</tr>
</tbody>
</table>

A (mole-cm$^3$-sec-K), $T_A$ (Kelvin)
The burning velocities obtained at $T_0 = 373$ K and $P = 1$ atm, with different rate coefficients are compared in Figure 3. Over all, the behavior of the burning velocity is similar for the rate coefficients from [3] and [7]. It appears that the burning velocity calculated with the rate coefficient from [11] is by far faster than the others. This is easily understandable with its pre-exponential factor of $6.32\times10^{11}$ which is five orders of magnitude higher than that from [7]. Because of the pre-exponential factor of $5.40\times10^5$, the burning velocity obtained with the rate coefficient from [3] is slightly below that obtained with the rate coefficient from [7] ($5.20\times10^6$). The burning velocity profiles obtained with the re-estimated rate parameters for reaction (1) from [8] are plotted at $T_0 = 373$K, and two pressures $P = 1$ and $P = 5$ atm in Figure 3, right. The results demonstrate that, apparently, the use of the re-estimated rate parameters considerably slows down the burning velocity by almost a factor of 1/10.

5. Species profiles

Figure 4 gives mole fraction profiles of SN (left) and NO (right) at $\lambda = 2.5, 1.0$ and 0.25. The calculated profiles exhibit that both SN and NO formation is strongly favored under stoichiometric conditions. This is in agreement with the flame temperature which at $\lambda = 1.0$ attains a maximum value. At $\lambda = 0.25$, SN formation is significantly lower but still observable, whereas NO formation at rich and lean conditions is negligible.

Acknowledgements

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Figure 3. Laminar burning velocity for $S_2$/air calculated with different rate coefficients for reaction (1), $T_0 = 373$ K and $P = 1$ atm, left. Laminar burning velocity for rate coefficient from [8], $P = 1$ and 5 atm, right.
Figure 4. Mole fraction profiles of SN and NO for $\lambda = 2.5, 1.0$ and 0.25

References


