INVESTIGATION OF S_2 + AIR COMBUSTION

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Abstract

This study comprises burning velocity calculations for the combustion of S_2 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 $S + O_2 \rightarrow SO + O$. 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 T_0 = 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 S_2 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 $S + O_2 \rightarrow SO + O$ are used. The effect of N_2 and O_2 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.

Table 1. N/S/O mechanism extracted from [7] and GRI [9].

Reactions from [7] A (mole-cm-sec-K), T_A (Kelvin)	$k = A \cdot T^b \cdot \exp(-T_A/T)$		
	A	b	T_A
1. $S + O_2 \leftrightarrow SO + O$	5.20E+06	1.8	-600.0
2. $S_2 + M \leftrightarrow 2S + M$	4.80E+13	0.0	38800.0
3. $S_2 + O \leftrightarrow SO + S$	1.00E+13	0.0	0.0
4. $SO_3 + O \leftrightarrow SO_2 + O_2$	2.00E+12	0.0	10000.0
5. $SO_3 + SO \leftrightarrow 2SO_2$	1.00E+12	0.0	5000.0
6. $SO + O(+M) \leftrightarrow SO_2 (+M)$	3.20E+13	0.0	0.0
7. $SO_2+O(+M) \leftrightarrow SO_3 (+M)$	9.20E+10	0.0	1200.0
8. $SO + M \leftrightarrow S + O + M$	4.00E+14	0.0	54000.0
9. $SO + O_2 \leftrightarrow SO_2 + O$	7.60E+03	2.4	1500.0
10. $2SO \leftrightarrow SO_2 + S$	2.00E+12	0.0	2000.0
11. $SO_3 + S \leftrightarrow SO + SO_2$	5.12E+11	0.0	0.0
12. $S + NO \leftrightarrow SN + O$	1.00E+12	0.5	17500.6
13. $N + SO \leftrightarrow NO + S$	6.31E+11	0.5	1010.3
14. $SN + NO \leftrightarrow N_2 + SO$	1.81E+10	0.0	0.0
15. $SN + O_2 \leftrightarrow SO + NO$	3.00E+08	0.0	0.0
16. $SN + NO_2 \leftrightarrow S + NO + NO$	4.07E+15	-1.0	0.0
17. $N + SN \leftrightarrow N_2 + S$	6.30E+11	0.5	0.0
18. $SO_2 + NO_2 \leftrightarrow NO + SO_3$	4.25E-19	8.9	3797.2
19. $SO + NO_2 \leftrightarrow SO_2 + NO$	8.43E+12	0.0	0.0
20. $SN + O \leftrightarrow SO + N$	6.31E+11	0.5	4030.6
Reactions from GRI [9]			
21. $N + NO \leftrightarrow N_2 + O$	2.70E+13	0.0	178.7
22. $N + O_2 \leftrightarrow NO + O$	9.00E+09	1.0	3271.3
23. $N_2O + O \leftrightarrow N_2 + O_2$	1.40E+12	0.0	5440.4
24. $N_2O + O \leftrightarrow 2NO$	2.90E+13	0.0	11650.7
25. $N_2O(+M) \leftrightarrow N_2 + O(+M)$	7.91E+10	0.0	28193.3
26. $NO + O \leftrightarrow NO_2$	1.06E+20	-1.4	0.0
27. $NO_2 + O \leftrightarrow NO + O_2$	3.90E+12	0.0	-120.8

2. Laminar burning velocities

Laminar burning velocities S_L have been calculated as a function of the air/fuel ratio λ. 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 < λ < 3.0. The airl/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.

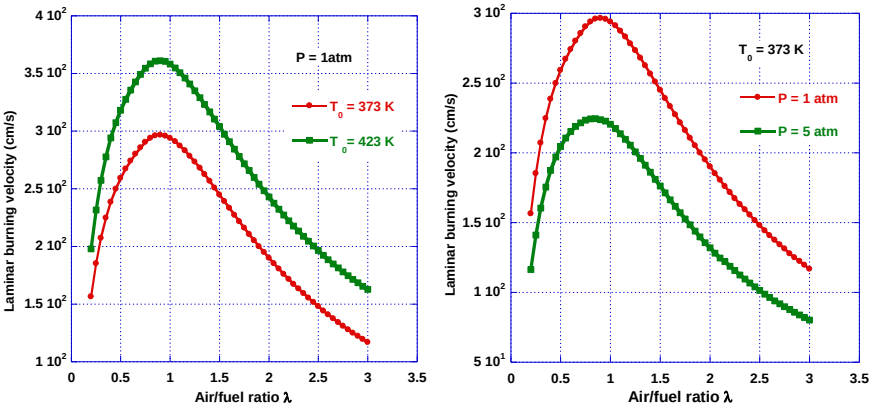

Figure 1. Laminar burning velocity for S_2/air calculated at two temperatures, T_0 = 373 K and T_0 = 423 K (left) and at two pressures P = 1 atm and 5 atm (right).

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 < λ < 1.0 (rich region) the flame speed increases to attain a maximum near 300 cm s^{-1} at λ = 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 λ = 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, λ = 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.

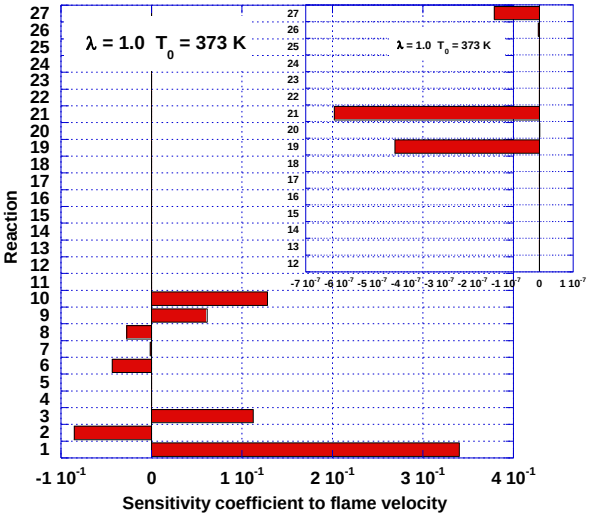

Figure 2: Sensitivity coefficients with respect to the burning velocity at stoichiometric conditions (λ = 1), T_0 = 373 K and P = 1 atm.

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 2. *Rate coefficients for reaction (1) from literature and own work for the flame calculations.*

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

A (mole-cm^3-sec-K), T_A (Kelvin)

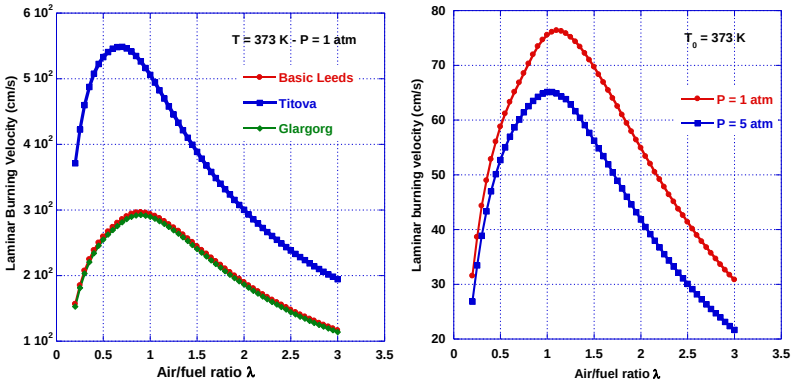

Figure 3. *Laminar burning velocity for S_2/air calculated with different rate coefficients for reaction (1), T_0 = 373 K and P = 1 atm, left. Laminar burning velocity for rate coefficient from [8], P = 1 and 5 atm, right.*

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 6.32×10^{11} which is five orders of magnitude higher than that from [7]. Because of the pre-exponential factor of 5.40×10^{5}, the burning velocity obtained with the rate coefficient from [3] is slightly below that obtained with the rate coefficient from [7] (5.20×10^{6}). The burning velocity profiles obtained with the re-estimated rate parameters for reaction (1) from [8] are plotted at T_0 = 373K, 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 λ = 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 λ = 1.0 attains a maximum value. At λ = 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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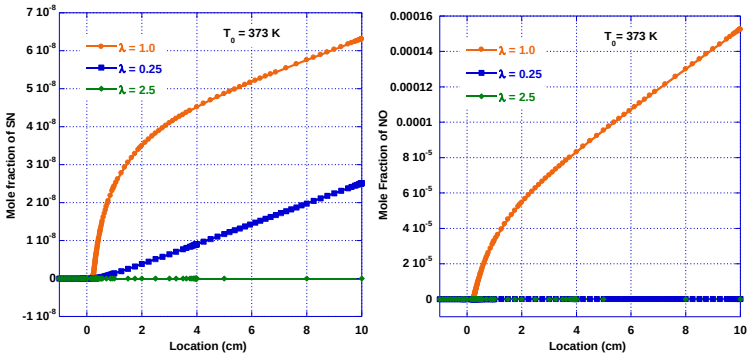

Figure 4. Mole fraction profiles of SN and NO for λ = 2.5, 1.0 and 0.25

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