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Experimental and kinetic modeling study of the CH₄+H₂S+air laminar burning velocities at atmospheric pressure



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ABSTRACT

With the increasing demand for natural gas and depletion of many sweet gas fields, direct usage of sour gas, usually containing a large percentage of hydrogen sulfide (H₂S), becomes a more economical choice in recent years. However, the laminar burning velocity (S_L) of CH₄+H₂S flames have seldom been investigated due to the corrosivity and toxicity of H₂S, and no available experimental data can be found for these mixtures burnt in the air. In this work, the laminar burning velocities of CH_4+H_2S+air flames were measured using the heat flux method at 1 atm and 298 K. The experimental data were obtained at various equivalence ratios and $x_{H2S} = 0-0.25$, where x_{H2S} refers to the mole fraction of H_2S in the fuel. Simulations using a detailed mechanism of Mulvihill et al. (2019) were carried out, showing good agreement with the present experimental results. Kinetic analyses of A-factor S_L reaction sensitivities, reaction pathways, and dominant intermediate species pointed out the importance of the C- and S-containing species interactions. To overcome the convergence problem of the Mulvihill mechanism, an examination of the unphysical reactions and species was carried out, which could be alleviated by making several reactions that violate the collision limit irreversible, accompanied by updating the heat capacity data. It's also found that substituting the hydrocarbon subset of the Mulvihill mechanism with mechanisms from FFCM-1, Konnov, San Diego, as well as Aramco noticeably deteriorates the simulation results due to the selection of different reaction rate constants.

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1. Introduction

Sour gas is one kind of natural gas that contains a noticeable amount of hydrogen sulfide (H_2S), as compared to the "sweet gas". For safety and efficiency reasons, the oilfield industries often "sweeten" the sour gas to reduce the acidic components before sending it to the end-users [1,2]. However, with the increase demanding of natural gas and depletion of many sweet gas fields in recent years, direct usage of sour gas becomes a more economical choice [3], and investigations are thus needed regarding the combustion properties of CH_4+H_2S , the main fuel component of sour gas.

The laminar burning velocity, S_L , is one of the most prominent properties in combustion research, which is helpful for the validation and updating of kinetic mechanisms. The S_L of CH₄ has been investigated extensively using various methods [4]; while due to its toxicity and corrosivity, the H₂S burning velocities were seldom studied. As summarized by Bongartz and Ghoniem [5], the scarce stoichiometric H_2S +air S_L data varied over 28–46 cm/s at 1 atm and 298 K, which in several studies was higher than the typical 35–38 cm/s for CH₄+air flame motivating the authors [5] to set target values of 42–46 cm/s for the burning velocities of H₂S+air flames used in their model optimization.

The CH₄+H₂S flames were investigated in the recent work of Mulvihill et al. [6]. However, H₂S diluted by Ar mixture was used by Mulvihill et al. [6] to supply the H₂S into experimental systems, thus the tested unburnt reactants are CH₄+H₂S+O₂+Ar with H₂S amount being always lower than 8.25% in the fuel mixtures CH₄+H₂S. Considering the prevailing usages of air in the industry as well as possibly varying H₂S amounts in sour gas [3], experimental data of CH₄+H₂S+air burning velocities are needed, especially with higher H₂S concentrations.

Compared with the extensively studied hydrocarbon systems, only a few kinetic mechanisms have been developed including the S reactions [7]. Mechanisms targeting the hydrocarbon+H₂S fueled systems are even rarer, e.g., the mechanisms from Bongartz and Ghoniem [5] and Gersen et al. [8]. Besides, the building targets of these hydrocarbon+H₂S mechanisms are ignition or flow reactor experiments, e.g., [9,10], not including the transport property data, and some of them didn't consider the fuel interactions [5], which

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Table 1Experimental conditions investi-
gated in the present study.

x _{H2S}	ϕ
0-0.25	1
0	0.7-1.4
0.075	0.7-1.4
0.15	0.7-1.3
0.225	0.7-1.2

has been proved important in the analysis of flame propagation [6]. To fill the gap, Mulvihill et al. [6] added a transport property file to the Gersen [8] mechanism, and incorporated adjustments of 17 key sulfur reactions from Mathieu et al. [11]. Thus, to the best of our knowledge, the Mulvihill mechanism [6] is the only available choice for predicting the CH_4+H_2S flame propagation. However, this mechanism was tested using limited burning velocity data in the Ar diluted flames without N₂, and significant convergence issues during the calculation processes were reported [6]. Validation (or even updating) of the mechanism using CH_4+H_2S+air flame data is needed. Also, thorough kinetic analyses could be applied to elucidate important reactions for the interactions between CH_4 and H_2S in the air environment, as well as to check out where the mechanism rigidity comes from.

Based on the above-mentioned background, the aims of the present study are: (1) to investigate experimentally the laminar burning velocity of CH_4+H_2S+air flames and compare it with simulation data using existing kinetic mechanism; and (2) to find out important interactions between CH_4 and H_2S in the air environment as well as ways to overcome the convergence problem.

2. Experimental setup

In the present experiments, the laminar burning velocities S_L of CH₄+H₂S+air flames were measured using the heat flux method at 298 K and 1 atm. The detail of experimental setup can be found in our previous publications [12–15].

The H₂S gas was supplied with 99.99% purity and was controlled using a corrosion-resistant mass flow controller. When the H₂S concentration in the unburnt mixture was high, unexpected black particle condensations were found on the burner plate surface. After polishing, the color of the brass plate turned from yellowish to purple. This phenomenon is attributed to the corrosivity of H₂S by reacting with Cu in the brass alloy, which peels off the original oxidation film and produces black solid compounds of CuS and/or Cu₂S. The change of burner plate color could also be understood since the exposed Cu turns purple quickly when oxidized by air. It should be noted that this phenomenon has not been reported in the literature experiments. One possible reason might be the high H₂S concentration conditions tested in the present work, and another possible reason could be the continuous consumption of unburnt mixture by burner stabilized flames, reinforcing the feature of condensation, as compared with transient consumption in spherical flames or shock tube measurements [6].

Since the good heat conductivity of brass is necessary for the heat flux burner measurement, the burner plate is not substituted by other corrosion-resistant materials. To avoid the catalytical effects on the flames, experimental results were only taken for the conditions without particle condensation conditions. Table 1 lists the present experimental conditions, where x_{H2S} refers to the mole fraction of H₂S in the CH₄+H₂S fuel mixture. The equivalence ratio ϕ is defined such that the complete combustion products are CO₂, H₂O, SO₂, and N₂.

The experimental uncertainty is evaluated in the same way as in our former studies [13,16], which considered two main uncertainty sources from the heat flux method measurements, i.e., uncertainties arising from the burner plate temperatures and gas flow rates. For most of the measured S_L in the present study, the evaluated uncertainty is within ± 1 cm/s. All the present S_L experimental data with the uncertainties are tabulated in the Supplementary Material.

3. Numerical calculation

All the kinetic modelings in the present study were performed with CHEMKIN-Pro-software [17]. The mechanism from Mulvihill et al. [6] was used. Reactions in the Mulvihill mechanism could be separated into 3 parts. i.e., (1) hydrocarbon subset from Hashemi et al. [18], with 69 species and 650 reactions, which has also been adopted by Glarborg mechanism [19]; (2) H₂S subset from Song et al. [20], where 17 reactions have been updated later by Mathieu et al. [11], containing 29 species and 277 reactions; and (3) interactions between C and S species from Gersen et al. [8], with 35 species and 299 reactions.

The effects of thermal diffusion (Soret effect), multicomponent transport, and radiative heat losses from CO, CO_2 , and H_2O [21] were taken into consideration. Grid independent results were obtained by setting the GRAD and CURV progressively to 0.02 and 0.05 during the calculation processes.

4. Result and discussion

4.1. Measured S_L of CH_4+H_2S+air flames

Figure 1 shows the present measured experimental burning velocity of CH₄+H₂S+air flames at 1 atm and 298 K, where panels (a) and (b) show respectively the stoichiometric S_L as a function of H_2S blending ratio x_{H2S} , and S_L at different x_{H2S} values as function of equivalence ratio ϕ . From Fig. 1, the laminar burning velocities decrease with the x_{H2S} increase from 0 to 0.25, and the difference caused by x_{H2S} is greater at fuel-rich side than that of fuel-lean side. Considering the target values of 42-46 cm/s burning velocities of H₂S+air flames adopted by Bongartz and Ghoniem [5], the blending of CH₄+H₂S disobeys the energy mixing rules discussed, e.g., in [15], inferring the non-negligible influence of fuel components interactions on the S_L , or highly uncertain measurements used in [5], which were reported more than 50 years ago. The results from Mulvihill et al. [6] were also included in Fig. 1(a), which possess the same decreasing trend with x_{H2S} while being lower than the present experimental data, since they used an O_2+Ar oxidizer different from air. Evaluation of the consistency of the present and Mulvihill et al. [6] data will be shown in Section 4.2.2, assisted by simulation results using different hydrocarbon subsets.

Figure 1 also shows simulation results using the Mulvihill mechanism. It should be noted that a similar convergence problem as discussed in [6] was also encountered in this study, while by long time and patient grid modifications, convergence was eventually achieved without changing any hydrocarbon reactions. From Fig. 1, one may conclude that the Mulvihill mechanism acceptably reproduces the present experimental S_L , except the slightly lower and higher predictions at x_{H2S} = 0 and 0.25, respectively.

4.2. Kinetic analyses

4.2.1. Analyses of the overall Mulvihill mechanism

To understand the fuel interactions in CH₄+H₂S+air flames, kinetic analyses were carried out, using the Mulvihill mechanism.



Fig. 1. Laminar burning velocities of CH₄+H₂S+air flames at 1 atm and 298 K.

Fig. 2(a) shows the top 10 reactions that have the largest absolute A-factor S_L sensitivities of the stoichiometric CH_4+H_2S+air flames. None of these reactions contain S species, indicating that the S_L predictions are mainly governed by hydrocarbon subset in the mechanism. This phenomenon is attributed to the limited amount of H_2S introduced in the present study, since when x_{H2S} grows to 1, the hydrocarbon reactions are irrelevant for the flame. In Fig. 2(a), sensitivity values of some reactions stay the same as x_{H2S} changing from 0 to 0.225, while the others vary with x_{H2S} . The latter reactions indeed govern the variation of burning velocity with x_{H2S} , which could be written as ζ_{xH2S} in Eq. (1), since the sensitivity difference between x_{H2S} and $x_{H2S} = 0$ conditions is equivalent to the sensitivity of ζ_{xH2S} , as shown in Eq. (2).

$$\zeta_{xH2S} = \frac{S_L(x_{H2S})}{S_L(x_{H2S} = 0)}$$
(1)

$$\operatorname{sense}_{\zeta_{X_{H2S}}}^{i} = \frac{\partial \ln\left(\zeta_{XH2S}\right)}{\partial \ln\left(k_{i}\right)} = \operatorname{sense}_{S_{L}(X_{H2S})}^{i} - \operatorname{sense}_{S_{L}(X_{H2S}=0)}^{i}$$
(2)

Based on this perception, Fig. 2(b) shows the top 10 reactions with the largest absolute ζ_{xH2S} sensitivities, which were derived using a homemade Matlab script. Among the important reactions shown in Fig. 2(b), 7 of them belong to the H₂S and C-S interaction reaction subsets, i.e., R1–R4 and R5–R7, respectively. By adjusting the rate parameters of these reactions within the uncertainty range, the ζ_{xH2S} or equivalently the slope of the S_L vs. x_{H2S} line can be tuned. Besides, the 3 hydrocarbon reactions in panel



Fig. 2. A-factor reaction sensitivities of the S_L and ζ_{xH2S} for CH_4+H_2S+air flames at 1 atm and 298 K.

(b) have all been present in panel (a), meaning that modifications in these reactions could tune the slope and the absolute value of S_L at the same time. The above categorization could be helpful for future mechanism updating.

$$SO_2+H(+M)HOSO(+M)$$
 (R1)

$$S+H_2SH+H$$
 (R2)

$$SO + O_2 SO_2 + O \tag{R3}$$

$$CH_3+SH=CH_3SH$$
 (R5)

$$CH_3SH + H = CH_3S + H_2 \tag{R6}$$

$$CH_3S + O_2 = CH_3 + SO_2 \tag{R7}$$

Figure 3 shows the reaction pathway analysis for the stoichiometric oxidation processes of CH_4+H_2S in the air with $x_{H2S} = 0.25$. The thickness of arrows in Fig. 3 represents the integrated rate of species production, and minor routes are neglected for the clarity of data presentation. The black arrows connect the C or S species separately, while the red color is used to denote the



Fig. 3. Reaction pathways of the stoichiometric CH_4+H_2S+air flames at $x_{H2S}=0.25$, 1 atm and 298 K.

C-S interaction reactions. On the left side of Fig. 3, CH₄ is oxidized mainly through CH₄->CH₃->CH₂O->HCO->CO->CO₂, with CH₂ and CH₂(S) branched from CH₃ forming CH₂O. On the right side of the plot, H₂S is oxidized through H₂S->HS->SO->SO₂ with reactions R1–R4 engaged, and part of the formed SO₂ recycles through the loop SO₂->HOSO->SO(S)->SO->SO₂. Since 75% of the fuel is CH₄, arrows representing the C routes are thicker than that of S. The interaction of C-S starts with CH₃ and HS forming CH₃SH (R5), which is converted to CH₃S through reactions R6 and R8, and finally by reaction R7, the consumption of CH₃S forms the CH₃ and SO₂, decoupling the C-S interaction.

$$CH_3SH+SH=H_2S+CH_3S$$
(R8)

Since reactions R1–R7 take part as dominant oxidation channels in Fig. 3, it's easy to understand their importance in the reaction sensitivities in Fig. 2. Except for CH₃SH and CH₃S, other C-S interactive species can also be found in the Mulvihill mechanism with a non-zero rate of production, e.g., CS₂, OCS, and CS. These species and the corresponding reactions are not shown in Fig. 3 only because their rates of production are lower than the set criterion when plotting the figure, i.e., 1E-5 mole/cm²s.

To elucidate important intermediate species in the C-S interactions, maximum concentrations of radicals are recorded, which are obtained at different positions in flames, and can thus indicate which radical becomes more important under different conditions. Fig. 4 shows the maximum mole fractions of OH, CH₃, and five Scontaining radicals with the maximum share in the flames studied, where panels (a) and (b) show respectively the stoichiometric and $x_{\text{H2S}} = 0.225$ conditions. To fit the plot, the data of OH and CH₃ mole fractions are divided by 5 and 2, respectively, and thus the labels "OH/5" and "CH3/2" are used. From Fig. 4, the 5 most important S-containing species in the $\text{CH}_4\text{+}\text{H}_2\text{S}\text{+}\text{air}$ flames are CHS, CH₃SH, CH₂S, SH, and CS₂, regardless of x_{H2S} or ϕ , and four of them are C-S intermediate species. The importance of CH₃SH has been shown in the reaction path analyses in Fig. 3, while the CHS, CH₂S, and CS₂ were not presented because of the smaller rate of production. It is noted that CH_3S , i.e., the other C-S intermediate species in Fig. 3, has a maximum mole fraction of 6E-5 over the conditions investigated, as a result of its fast formation and con-



Fig. 4. Maximum mole fractions of intermediate species in CH_4+H_2S+air flames, at 1 atm and 298 K.

sumption. This maximum mole fraction number is only 20% of the bottom species CS_2 , therefore it is not shown in Fig. 4.

The present kinetic analyses are restricted by the small x_{H2S} conditions in the experiment, while predictions can also be made by the Mulvihill mechanism on the $x_{H2S} > 0.25$ performance. These explorations were put to the Supplementary Material, where the importance of C-S interactions is predominant around $x_{H2S} = 0.5$, making the burning velocity smaller than under the pure CH₄ and H₂S conditions. The predicted laminar burning velocity, reaction sensitivity, as well as dominant intermediate species can be found in Figs. S1-S3.

4.2.2. Influence of the hydrocarbon subset

Facing the convergence problem in the flame simulations, Mulvihill et al. [6] mentioned that substituting the hydrocarbon reactions by the AramcoMech 1.3 [22] largely helps the convergence, therefore, several widely used hydrocarbon mechanisms were selected in the present study to check their compatibility with the Mulvihill mechanism. These mechanisms are FFCM-1 [23], Konnov (version released by Capriolo et al. [24]), San Diego [25], as well as AramcoMech [22]. It should be noted that the lowtemperature species CH₃OO and CH₃OOH react with HS through reactions R9 and R10 in the Mulvihill mechanism, while these



Fig. 5. Predictions of stoichiometric CH_4+H_2S+air flame burning velocities at 1 atm and 298 K.

Table 2

Rate constant differences in the most sensitive reactions in Fig. 2, compared with those in the Mulvihill mechanism.

Reactions	San	FFCM	FFCM Konnov	
H +02=0+0H	0.10	-0.02	0.04	0.04
$CH_3+H(+M)=CH_4(+M)$	0.19	-0.19	0.02	-0.57
HCO(+M)=H+CO(+M)	2.50	0.64	3.61	4.53
CO+OH=CO ₂ +H	0.73	0.58	1.04	0.80
$H + O_2(+M) = HO_2(+M)$	0.34	0.32	0.34	0.34
$CH_2O+H = H+CO+H_2$	-	-	0.00	-
CH ₄ +H=CH ₃ +H ₂	0.00	-0.54	-0.41	-0.41
CH ₂ O+H=HCO+H ₂	0.30	0.63	0.00	0.31
$OH+H_2=H+H_2O$	0.10	0.10	0.13	-0.09
$HCO+O_2=CO+HO_2$	-0.62	-0.75	0.00	-1.00

species are not available in the mechanisms of FFCM-1 and San Diego, thus reactions R9 and R10 are deleted in the corresponding combinations.

 $CH_{3}OO+SH=HSO+CH_{3}O$ (R9)

$$CH_3OOH+SH=CH_3OO+H_2S$$
(R10)

Effects of these hydrocarbon subsets on the stoichiometric $CH_4+H_2S+air S_I$ predictions are shown in Fig. 5. Convergence is more easily achieved using the combinations with FFCM-1, and San Diego mechanisms, since they have fewer species and reactions. However, none of the checked combinations reproduce better the experimental data than the original Mulvihill mechanism, even the combination with AramcoMech 1.3 suggested by Mulvihill et al. [6]. Since the H₂S and C-S subsets used are all the same in Fig. 5, the differences in the predictions should be caused by the sensitive reactions in the hydrocarbon subsets, as those shown in Fig. 2. It is found that the most sensitive reactions are almost the same for the different mechanisms, while the sensitivity values and rank orders are slightly different. Table 2 shows the rate constant differences of the 10 most sensitive reactions among different mechanisms, where the listed reactions follow the same order as in Fig. 2(a), and the differences were derived as (substituted mechanism/Mulvihill mechanism - 1). From Table 2, all the reactions, except R11 and R12, have noticeable differences in the rates of sensitive reactions. Therefore, the divergent predictions in Fig. 5 by different mechanisms can't be blamed on one or a couple of reactions, indeed, they are caused by the very different selections in the whole hydrocarbon scheme.

$$H+O_2=O+OH \tag{R11}$$

$$OH + H_2 = H + H_2 O \tag{R12}$$

Based on the above findings, the hydrocarbon subset in the Mulvihill mechanism should not be substituted by other mechanisms for the accuracy of prediction. It should also be noted that the simulations in Mulvihill et al. work [6], i.e., substituting the hydrocarbon subset from Aramco, are approximately 2 cm/s higher than the experimental data at stoichiometric $x_{H2S} = 0.085$ condition. From present Fig. 5, the present experimental data are also around 2 cm/s lower than simulation using the Aramco subset. Therefore, the present experiment is expected to be consistent with Mulvihill et al. [6].

4.3. Solution to the convergence issue

From the last section, substituting the hydrocarbon subset of the Mulvihill mechanism results in degraded prediction accuracy, and therefore, a solution to the convergence issue is still needed. Generally, the convergence issue of a mechanism arises from the model stiffness, caused by unphysical reactions and thermodynamic data. In addition, the large size of the model can result in large CPU cost and makes it difficult to find out proper grid settings. Therefore, the solution to the convergence issue should lie in dealing with unphysical mechanism parameters, while reducing the mechanism size may also help. These issues will be discussed in the following.

4.3.1. Unphysical reactions and thermodynamic data

The main numerical problem of the Mulvihill mechanism is unphysical thermodynamic data of two species: CH_2S_2 and HSOO, which have negative heat capacity c_p .

In the Mulvihill mechanism, the thermodynamic data of the HSOO species are from Zhou et al. [26], fitting heat of formation calculations in their early work [27]. The c_p data first increase with temperature and non-monotonically decrease after 3000 K, while negative values are observed above 4000 K, much higher than the flame temperature. Since Zhou et al. [26] didn't report the upper limit of fitting temperature, the high-temperature range of the HSOO NASA polynomial coefficient is manually changed from 1000–5000 K to 1000–3000 K, thus excluding negative c_p in the flame calculation.

The thermodynamic data of CH_2S_2 species refer to the theoretical work from Vandeputte et al. [28], where the tabulated heat capacity data from 300 K to 1500 K as well as the NASA polynomials can be found. In [28], the tabulated c_p data of CH_2S_2 monotonically increase with temperature, while that derived using NASA polynomial coefficients has decreasing tendency from 1000 K, leading to the negative c_p for temperature higher than 1800 K. Therefore, the NASA polynomials of CH_2S_2 are refitted in this work using the tabulated c_p data, with a manually extrapolated 2000 K point added to avoid negative c_p within the flame temperature range. It should be noted that the enthalpy and entropy derived using the original fitting coefficients are not changed. The updated c_p fitting data are compared with the original tabulated and fitting data in Fig. 6.

Besides, examination of the Mulvihill mechanism reveals that the rate constants of several reactions in the reverse direction violate the collision limit [29]. Specifically, the following S-containing reactions (R13–R16) and hydrocarbon reactions (R17–R22), have reverse rate constants exceeding 10^{20} cm³/mole·s at low temperatures:

$$SO+M = S+O+M \tag{R13}$$

$$HSO+O_2 = HSO_2 + O \tag{R14}$$



Fig. 6. Comparison of the updated CH_2S_2 heat capacity fitting results with the original tabulated and fitting data from Vandeputte et al. [28].

 $CS_2 + SO = CS + S_2O$ (R15)

OCS+M=CO+S+M(R16)

 $CH_3 + M = CH + H_2 + M \tag{R17}$

 $CH_3 + M = CH_2 + H + M \tag{R18}$

 $CH_2+M=CH+H+M$

 $CH_2 + M = C + H_2 + M \tag{R20}$

 $C_2H_2+M = C_2H+H+M$ (R21)

$$C_2 O + M = C + C O + M \tag{R22}$$

An easy option to alleviate this problem is just making the violating reactions irreversible, since it has been demonstrated [30] that if the reactions thus modified are not in the list of the most sensitive ones, the calculated burning velocity is very close to that obtained with the unmodified model. Note, that reactions R17–R22 in the Konnov mechanism [24] were already made irreversible as recently described by Alekseev et al. [31], while the reactions are even neglected in the FFCM-1, San Diego, and AramcoMech mechanisms. This can explain why the hydrocarbon substitution in Section 4.2.2 makes the convergence easier.

However, the convergence issues are not only met when modeling the flame propagation, and the underlying reasons should be linked to either wrong thermodynamics data or wrong rate constant expressions. It's noted that all the species in R13-R22 adopted contemporary thermodynamic data such as from the Burcat database (2016) [32], and since these species also participate in many other reactions without trouble, the violation of the collisional limit should be mainly attributed to the wrong rate expression. Table 3 lists the information for the R13-R22 reactions, where the temperature ranges for the rate expressions are all much higher than 300 K, except for the R15 reaction where the temperature range was not specified. The accuracy of the lowtemperature rate constants is thus difficult to ensure using the fitted high-temperature results. Therefore, refitting of the rate expression was made in the present work that includes the original high-temperature data and an estimated reverse rate constant



Fig. 7. Rate constant for reaction R13, present fitting compared with the experimental data and fitting from Plach et al. [33].



Fig. 8. Relative differences in the reduced mechanisms and their predictions, compared with the Mulvihill mechanism.

of 1E18 at 300 K, to avoid exceeding the collisional limit at low temperatures while keeping the high-temperature rate constants. The forward rate constants at 300 K are much smaller than at the high temperatures, and its influence is easily to be ignored in the direct fitting of $k = AT^b \exp(-\frac{E_a}{RT})$. To deal with this difficulty, the logarithmic format of the modified Arrenius equation was used instead, which increases the weight of the 300 K data. Fig. 7 shows the suggested rate expression fitting of reaction R13 as an example, and all the present fitting results are tabulated in Table 3.

To compare with the original Mulvihill mechanism, the modification with updated reactions R13–R22 rate expressions and updated heat capacities is labeled "Model 1". Its performance on the laminar burning velocity as well as ignition delay times will be shown in Section 4.3.2. The model reduction was also made based on Model 1, producing a Model 2 without low-temperature reactions and a further reduced Model 3, which is explained in detail in the Supplementary Material.

4.3.2. Performance of the updated mechanisms

Figure 8 shows specific differences between the new models and the original Mulvihill mechanism, i.e., the numbers of species and reactions in the mechanism, and the averaged CPU

(R19)

Table 3

Information on the reactions violating the collisional limit in the Mulvihill mechanism and the updated expressions. Type referring to the data used for the original fitting from Exp.-experiment, Rev.-review, and Est.-estimation; units in cal, mol, cm, and s.

No	Original rate expression information					Present updated			
	T(K)	А	b	Ea	Туре	Ref.	A	b	Ea
R13	3000-5000	4.00E14	0	1.07E05	Exp.	[33]	4.40E20	-1.45	1.22E05
R14	1000-1500	8.40E-07	5.1	1.13E04	Est. *	[34]	5.42E13	-0.52	2.49E04
R15	-	1.00E12	0	1.0E04	Est.**	[35]	1.37E24	-3.38	1.95E04
R16	1900-3230	2.50E14	0	6.14E04	Exp.	[36]	1.23E19	-1.23	6.74E04
R17	2706-3527	3.10E15	0	8.09E04	Exp.	[37]	1.08E30	-3.59	1.09E05
R18	2253-2975	2.20E15	0	8.27E04	Exp.	[37]	9.33E38	-6.08	1.16E05
R19	1900-2700	5.60E15	0	8.90E04	Exp.	[38]	1.62E27	-3.05	1.02E05
R20	2400-3800	5.80E12	0.5	6.85E04	Rev.	[38]	2.57E16	-0.43	7.41E04
R21	700-2500	9.10E30	-3.7	1.27E05	Rev.	[39]	5.16E52	-9.68	1.44E05
R22	1785-2270	2.00E15	0	4.42E04	Exp.	[40]	4.22E07	2.39	4.62E04

*: the rate expression for R14 was estimated by Rasmussen et al. [34] according to ab initio CBS-QB3 calculations combined with transition state theory (TST).

**: the rate expression for R15 was a pure estimation with analogous reactions by Glarborg et al. [35], and there is no temperature range specified for the estimation.



Fig. 9. Predictions of the new models against CH_4+H_2S burning velocities and ignition delay times. The ignition delay time experimental data from Mulvihill et al. [6].

time needed for the calculations. Averaged differences in predicting the stoichiometric CH_4+H_2S+air flames with $x_{H2S} = 0-0.25$ are also shown, which focus on the burning velocities and maximum mole fractions of dominant intermediate species in Fig. 4 (OH, CH₃, CHS, and CH₃SH). The shown difference values in Fig. 8 were eval-

uated in a relative way, which is (value of new model/value of the Mulvihill mechanism - 1).

From Fig. 8, the average CPU time using Model 1 decreases by 90% from the original Mulvihill mechanism, with negligible differences in the stoichiometric CH₄+H₂S+air flame predictions. For the further reduced mechanisms, it is seen that with the numbers of species and reactions decreasing by 13% and 35% for Model 2 and Model 3, the CPU time further decreases by 3% and 6%, respectively. The differences originated from the mechanism reduction in the stoichiometric S₁ and maximum OH as well as CH₃ mole fractions are hardly noticeable, while up to a 5% increase is found in the reduced mechanism predictions for the maximum CH₃SH and CHS mole fractions. It should be noted that Model 3 (84 species and 786 reactions) could be further reduced using different methods, however, similar but larger deviations as the CHS and CH₃SH mole fractions are expected, and the CPU cost has already reached an acceptable level, thus the calculations were not carried out in the present work.

Figure 9 shows the predictions of Models 1, 2, and 3 at conditions other than the stoichiometric burning velocities. Panel (a) shows the $x_{H2S} = 0$ and 0.225 burning velocities for the CH₄+H₂S+air flames, as a function of ϕ . Panel (b) shows the ignition delay times of 0.0638% H₂S+0.1492% CH₄+0.787% O₂+99%Ar mixture, where the experimental data are from Mulvihill et al. [6]. From Fig. 9, predictions of the new models all overlap with the original Mulvihill mechanism under all the investigated conditions, indicating their capability in reproducing the original mechanism performances.

5. Conclusion

In this work, the laminar burning velocities S_L of CH_4+H_2S+air flames were measured using the heat flux method at 1 atm and 298 K. The experimental data were obtained at $x_{H2S} = 0-0.25$, which has not yet been investigated in the literature and could be useful for the kinetic mechanism validation. Simulations using the detailed Mulvihill mechanism were carried out, and results with no modifications in the hydrocarbon reactions were obtained, showing good agreement with the present experimental data.

Kinetic analyses using the Mulvihill mechanism were made, covering the A-factor reaction sensitivities of the burning velocities, integrated rate of productions, and maximum mole fractions of dominant intermediate species in the CH_4+H_2S+air flames. These results reveal important species and reactions for the investigated flames, especially the interactions between the C- and S- containing species. The solution to the convergence problem of the Mulvihill mechanism was proposed, by updating the unphysi-

cal thermodynamic data of species CH_2S_2 and HSOO, as well as refitting the rate expressions for reactions violating the collision limit in the reverse direction. Mechanism reductions were also carried out to further decrease the computational CPU time while reproducing the Mulvihill mechanism predictions on the burning velocities, maximum species mole fractions, and ignition delay times of CH_4+H_2S mixtures. It's also found that substituting the hydrocarbon subset of the Mulvihill mechanism with the mechanisms from FFCM-1, Konnov, San Diego, as well as AramcoMech deteriorates the simulation results noticeably.

Besides, CuS or Cu_2S condensations were found when measuring the high H_2S composition conditions, which is attributed to the corrosive H_2S reacting with surface Cu in the brass alloy. This phenomenon is conspicuous in the present burner stabilized flame setup, and it is suggested to check carefully in future experiments using different setups, thus avoiding possible catalytical effects of the formed particles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2022. 112288.

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