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Impact of carbon dioxide and nitrogen addition on the global structure of hydrogen flames

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2 **Impact of carbon dioxide and nitrogen addition on the**

3 **global structure of hydrogen flames**

4

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6

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14

15 **Abstract**

16 Investigations into the combustion characteristics and flame structure of hydrogen/air flames with  
17 different dilutions of hydrogen with carbon dioxide have been carried out experimentally and numerically.  
18 The aim was to determine the variations of the flame shape for different carbon dioxide dilutions in the  
19 H<sub>2</sub>-air mixtures. For this purpose, premixed flames at various compositions of hydrogen-carbon dioxide  
20 mixtures are investigated experimentally in a heat flux burner configuration at varying equivalence ratios  
21 from 0.5 to 1.1, fresh gas temperatures and under atmospheric conditions. Optical investigations are  
22 performed to detect the number of cellular structures on the flame front. Furthermore, the laminar  
23 burning velocity and the influence of carbon dioxide addition were examined numerically. A detailed  
24 kinetic mechanism was implemented for the identification of the most representative intermediates via  
25 a reaction path analysis, and the most influential species and reactions are identified through sensitivity  
26 analyses at conditions relevant to the studied application. Considering the nature of the adopted  
27 mechanism, the presence of CO<sub>2</sub> has the potential to shift the production/consumption rate of some  
28 hydrogen-containing radicals. Hence, numerical investigations employing an inert species having the  
29 same thermodynamic and transport properties as CO<sub>2</sub> (referred to as fictitious CO<sub>2</sub>, FCO<sub>2</sub>) were

30 compared and discussed in this work. To investigate the effect of CO<sub>2</sub> on the dynamics of the hydrogen  
31 flames, one-dimensional and two-dimensional detailed simulations of the flame structure have been  
32 carried out. The addition of CO<sub>2</sub> makes the flame more prone to thermo-diffusive instabilities through a  
33 decrease in the mixture's thermal diffusivity. This results in a decrease of the Markstein number and an  
34 enhanced formation of characteristic cellular structures on spherically expanding flames. Overall the  
35 comparison between the experimental and numerical investigations reveals similar conclusions.

36

37 Keywords: hydrogen admixtures, flame structure, CO<sub>2</sub>, cellular structures

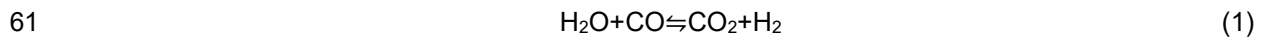
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## 39 **Introduction**

40 To reduce CO<sub>2</sub> emissions, fossil fuels, such as natural gas, have to be replaced in the gas supply  
41 system by non-fossil energy carries, such as hydrogen produced preferably from renewable sources. In  
42 this context, carbon oxides as by-products from hydrogen manufacturing are an increasingly important  
43 issue in the utilization of lower grade hydrogen. Technologies needed for the industrial utilization of  
44 hydrogen, e.g. safe transport and optimised combustion, are under rapid development or in the  
45 prototype stadium. Numerous industrial thermo-processes could run on gaseous mixtures rich in H<sub>2</sub> and  
46 CO<sub>2</sub>, including hydrogen from biomass conversion, plastic waste treatment, thermal processes, steam  
47 reforming, and gasification processes [1]. Undoubtedly, new technologies based on H<sub>2</sub> for providing of  
48 energy (e.g., integrated gasification combined cycle or gas turbines) have been considerably improved  
49 in the last decades for reduction of air pollution. Commonly, a large variety of processed materials or  
50 operating conditions can be applied for these processes. For example, steam reforming and gasification  
51 can implement different charges (e.g., methane, naphtha, or coal) and have several target products  
52 (e.g., hydrogen, methanol, or ammonia), resulting in considerably different compositions of the product  
53 stream from the reactor (see Table 1, adapted from [2,3]).

54 These product streams usually are treated via several conversion and separation processes aiming  
55 at the reduction of impurities (e.g., sulphur-based species) and undesired by-products. Considering that  
56 95 % of H<sub>2</sub> is produced via steam reforming worldwide [1], particular attention is paid to the conversion  
57 of CO when H<sub>2</sub> is manufactured for providing of energy. In this case, shift reactors are commonly  
58 integrated into the process to convert CO (Equation 1), with obvious implications on the H<sub>2</sub> to CO<sub>2</sub>

59 volume ratio. Based on data reported in refs [1-4] for the ratio of H<sub>2</sub>/CO for gasification processes, a  
 60 proper amount of steam must be provided.



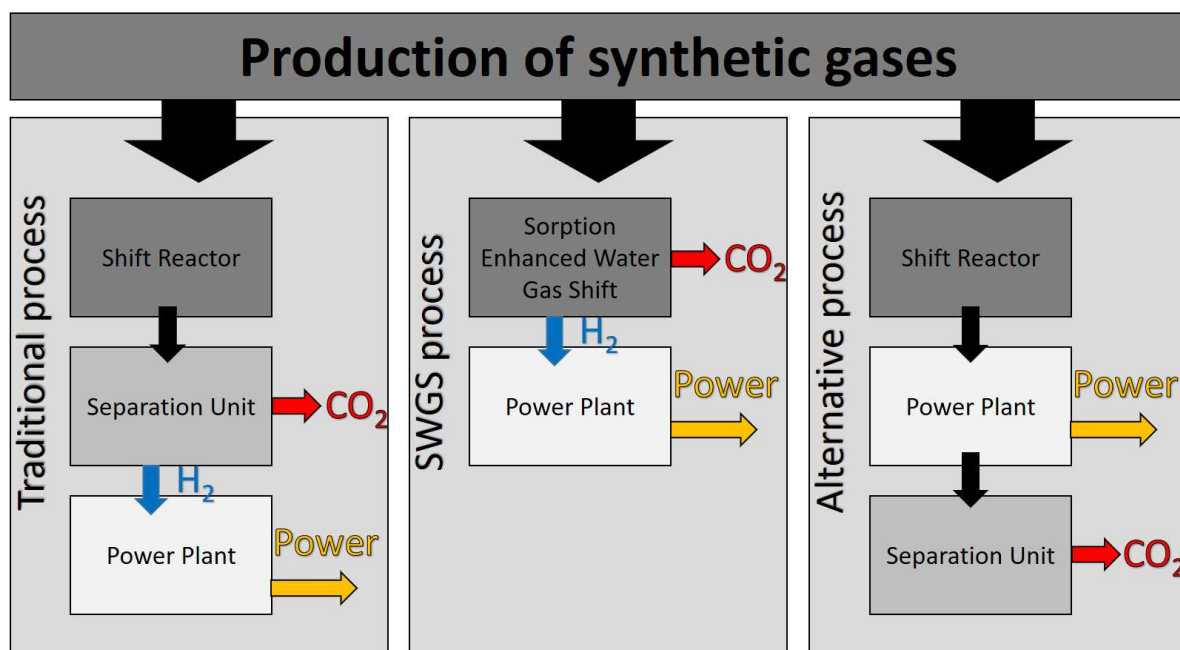
62  
 63 **Table 1** Typical composition of products gases from industrial processes delivering gaseous  
 64 mixtures rich in H<sub>2</sub> and CO<sub>2</sub>. Adapted from [2,3]

Process	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O	H <sub>2</sub> /CO <sub>2</sub>	C/H
SR (Methane)	48.6	9.2	5.2	5.2	31.8	9,35	0.12
SR (Nafta)	34.6	5.3	8.0	8.0	44.1	4.33	0.14
MBG (Coal)	52.2	29.5	5.6	4.4	5.1	9.32	0.34
FBG (Coal)	27.7	54.6	4.7	5.8	4.4	5.89	1.01
EFG (Goal)	26.7	63.1	1.5	0.03	2.0	17.80	1.13

65 SR = Stream reforming, MBG = Moving Bed Gasifier, FBG = Fluidized Bed Gasifier, EFG = Entrained Flow Gasifier

66  
 67 Traditionally, a separation unit is employed to produce the H<sub>2</sub>-rich stream for power generation and CO<sub>2</sub>  
 68 for carbon sequestration. More recently, investigations have suggested the re-use of sequestered CO<sub>2</sub>  
 69 as fracking agent [4]. Alternatively, the integration of water gas shift reactors and separation in a single  
 70 unit has been intensively studied and referred to as sorption enhanced water gas shift (SEWGS) [5,6].  
 71 Dealing with highly pure H<sub>2</sub> streams raises concerns of safety during storage and transportation [7], and  
 72 poses new challenges for environmental and technological aspects during combustion [8], e.g.  
 73 production of pollutants such as NO<sub>x</sub> [9]. On the other hand, the presence of CO<sub>2</sub> in the streams resulting  
 74 from shift reactors offers alternative technological solutions utilizing its effects as a thermal diluent.  
 75 Indeed, the use of CO<sub>2</sub> has been recently considered within the energy supply chain either as a service  
 76 fluid for indirect heat transfer or as a component in the combustion chamber for direct heat transfer [10].  
 77 The latter approach includes Allam's Cycle [11] and it can be intended as an integrated strategy to  
 78 recycle the CO<sub>2</sub> deriving from the carbon capture units and reduce the technical requirements. However,  
 79 if traditional, carbon-based fuels are considered, the presence of CO<sub>2</sub> alters the chemical equilibrium,  
 80 limiting the fuel conversion being a final product already present in the mixture. This drawback is

81 implicitly erased in the case of H<sub>2</sub>-CO<sub>2</sub> mixtures. With these premises, direct combustion of H<sub>2</sub>-CO<sub>2</sub>  
82 followed by carbon sequestration may be considered as a possible alternative, see Figure 1.



83 **Figure 1** Schematic representation of synthetic gas-based processes

84 Quantitative investigations on the chemistry of combustion and flammability limits of H<sub>2</sub>/CO<sub>2</sub>-  
85 mixtures are missing at present. Indeed, most of the published studies dealing with the combustion  
86 chemistry of binary mixtures of C<sub>0</sub>-C<sub>1</sub> species were devoted to the characterization of the interactions  
87 between CO and H<sub>2</sub> [12,13] in the view of synthetic gas utilization, or CH<sub>4</sub> and H<sub>2</sub> [14,15] for the  
88 application of hydrogen enriched methane flames [16]. The chemistry of H<sub>2</sub>-CO<sub>2</sub> in complex mixtures  
89 was investigated as per the employment of oxygen-enriched air or pure oxygen [17] or in the case of  
90 biomass-derived fuels [18–21]. For safety relevant aspects, the effects of CO<sub>2</sub> addition on the hydrogen  
91 ignition limits were characterized by Djebaili et al. [22] at high temperatures, revealing the existence of  
92 non-thermal inhibition of the hydrogen oxidation.

93 The laminar burning velocities (LBV) of H<sub>2</sub>/CO<sub>2</sub>- mixtures were investigated at different temperatures  
94 and mixture compositions. For diluted H<sub>2</sub>-air mixtures, planar flames formed in diverging channels could  
95 be used for the measurement. The effect of CO<sub>2</sub> is stronger than that of N<sub>2</sub> in reducing the burning  
96 velocity indicating a thermal and chemical effect of CO<sub>2</sub> dilution [23,24]. However, no apparent influence  
97 on the morphology of the planar flame due to the CO<sub>2</sub> admixture is reported. In other studies with flat  
98 flames, cellular structures were observed in CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>2</sub>H<sub>6</sub> flames [25] with high CO<sub>2</sub> dilution. Also  
99 in flat flames stabilised on a McKenna burner, instabilities were observed in extremely lean CH<sub>4</sub>-H<sub>2</sub>-CO<sub>2</sub>

100 flames with equivalence ratios of  $\phi = 0.55-0.69$ . Beyond that, no further studies on instabilities of the  
101 flame front due to the admixture of  $\text{CO}_2$  are known [26]. The occurrence of cellular instabilities in  
102 adiabatic  $\text{H}_2/\text{O}_2/\text{N}_2$  premixed flames anchored to a heat flux burner has been investigated numerically.  
103 Both hydrodynamic instabilities and diffusional instabilities leading to the formation of cellular flames  
104 were studied [27]. An adiabatic unstretched planar flame anchored to the heat-flux burner could only be  
105 realized within a critical lift-off distance. This lift-off distance seems to differ for each mixture. To explain  
106 the occurrence of these phenomena in more detail, insights from experimental and numerical  
107 investigations are necessary.

108 In this paper,  $\text{H}_2\text{-O}_2\text{-N}_2\text{-CO}_2$  flames were investigated numerically to elucidate the effect of  $\text{CO}_2$   
109 dilution on combustion properties, flame structure and instabilities. The effects of  $\text{CO}_2$  dilution on laminar  
110 burning velocity and Markstein length are investigated and quantified with 1-D simulation results using  
111 different reaction mechanisms. Further, the effects of  $\text{CO}_2$ -dilution on flame structure were investigated.  
112 Significant changes in flame morphology were found in experiments with  $\text{H}_2\text{-O}_2\text{-N}_2\text{-CO}_2$  flames stabilized  
113 on a heat flux burner. The results were quantified as a function of plate temperature, unburned gas  
114 velocity and equivalence ratio. 2-D numerical simulations served to explain the appearance of the  
115 formation of cellular structures in the investigated flames.

116

## 117 **1-D and 2-D Simulations, Numerical Setup and Procedure**

118 Laminar burning velocity is generally considered a stand-alone parameter summarizing the  
119 interaction of convection, diffusion and chemical reactions during combustion [28]. In this work, the  
120 laminar burning velocity was estimated through the numerical simulation of one-dimensional, freely  
121 propagating, and adiabatic flames with the open-source software Cantera [29]. Absolute and relative  
122 tolerances for the steady-state problem were set to  $1.0 \cdot 10^{-9}$  and  $1.0 \cdot 10^{-4}$ , respectively. Additional  
123 information about the numerical setup and adopted procedure can be found elsewhere [30].

124 Several strategies for the development of detailed kinetic mechanisms can be used, including manual  
125 enlargement or automatic generation [31]. The selected strategy as well as the approach adopted to  
126 produce thermodynamic and kinetic data to be used as input strongly affect the laminar burning velocity  
127 predicted by the produced mechanisms, as recently demonstrated [32]. Nevertheless, the identification  
128 of the most accurate model for the hydrogen case is still a challenging task. Indeed, a comparison of  
129 the experimental measurements for the laminar burning velocity of hydrogen-containing mixtures from  
130 different setups shows a significant variability of this parameter [33]. On the other hand, it is worth

131 mentioning that all predictions can be included in the uncertainties range typically associated with the  
 132 laminar burning velocity measurements [34]. Eventually, the tendency of GriMech3.0 in underestimating  
 133 the overall reactivity has been already reported for low-carbon fuels [35].

134 A detailed kinetic mechanism composed of ~80 species and ~600 reactions, referred to as KiBO  
 135 (Kinetics in Bologna) was employed because of the verified accuracy in reproducing the combustion  
 136 chemistry of light species [28]. The initial temperature of  $T_{\text{gas}} = 298$  K and atmospheric pressure were  
 137 considered. Several combustible mixture compositions were tested, varying the equivalence ratio  
 138 between  $\phi = 0.5 - 6.0$  and the  $\text{H}_2/\text{diluent}$  ratio by moles from 1.0 - 6.0. Either  $\text{CO}_2$  or  $\text{N}_2$  was used as  
 139 diluent. The same conditions were used for fictitious  $\text{CO}_2$  (i.e.,  $\text{FCO}_2$ ), as well.  $\text{FCO}_2$  is an artificial  
 140 species with the same thermodynamic and transport properties as  $\text{CO}_2$ , but not involved in any reaction.

141 A sensitivity analysis is performed by imposing a perturbation equal to 0.1 % of each input parameter  
 142 (i.e., the rate constant of the  $i$ -th reaction,  $k_i$ ) and evaluating the effects on the LBV. Results are  
 143 expressed as normalized sensitivity coefficients ( $NSC$ ), defined in Equation 2,

$$144 \quad NSC = \left( \frac{k_{i,0}}{s_{L,0}} \right) \cdot \frac{\partial s_L}{\partial k_i} \quad (2)$$

145 where the subscript 0 denotes the unperturbed values

146 Reaction path analysis identifies the key intermediates in the reaction path and quantifies the relative  
 147 weight of each branch by estimating branching ratios. The relative width of the connection pathway is  
 148 related to the relative contribution of the pathway to the species net yield [36]. In this work, a global  
 149 pathway selection algorithm is implemented in a zero-dimensional constant volume system to identify  
 150 the shortest paths connecting the most relevant species involved in the element flux. A threshold value  
 151 of 0.01 is adopted for the selection of species to be included in the analysis. This approach allows for  
 152 the generation of overall reaction paths. Hence, results are independent of the time instance, in contrast  
 153 to the traditional path flux algorithm. Considering the analysed mixtures, the migration of H is  
 154 investigated. Additional details of this methodology can be found in the references [37,38].

155 The effect of carbon dioxide dilution of hydrogen on possible thermo-diffusive instabilities is  
 156 numerically investigated using one-dimensional and two-dimensional flames. In this context, the  
 157 Markstein number  $Ma$  expresses how sensitive the burning velocity  $s_L$ , normalized by the flame speed  
 158 of an unstretched flame  $s_{L,0}$ , is to the dimensionless flame stretch or Karlovitz number  $Ka$ :

$$159 \quad Ma := - \frac{\partial s_L / s_{L,0}}{\partial Ka} \quad Ka := \frac{1}{A} \frac{dA}{dt} \frac{d_{fL0}}{s_{L,0}} \quad (3)$$

160 where  $d_{fl,0}$  is the thermal thickness of the unstretched flame front. A negative Markstein number is  
161 generally indicative of thermo-diffusively unstable flames. To quantify the Markstein number of hydrogen  
162 flames with different fuel dilutions, numerical simulations of counterflow-twin flames are performed with  
163 the open-source library Cantera [29]. In this axisymmetric setup, two opposed nozzles in 5 cm distance  
164 serve as inlets of the premixed hydrogen-dilutant-air mixture at atmospheric conditions with a prescribed  
165 velocity. The oxidizer is air and the fuel is a mixture of hydrogen and the dilutant. In all cases, the  
166 equivalence ratio is  $\phi = 0.9$ . The diffusion model is the mixture-averaged model applying the  
167 Hirschfelder-Curtiss approximation, thereby taking preferential diffusion into account.

168 Lastly, a detailed 2-D simulation of a spherically expanding flames is conducted to study the  
169 evolution of cellular structures on the thermo-diffusively unstable flame during flame propagation.

170

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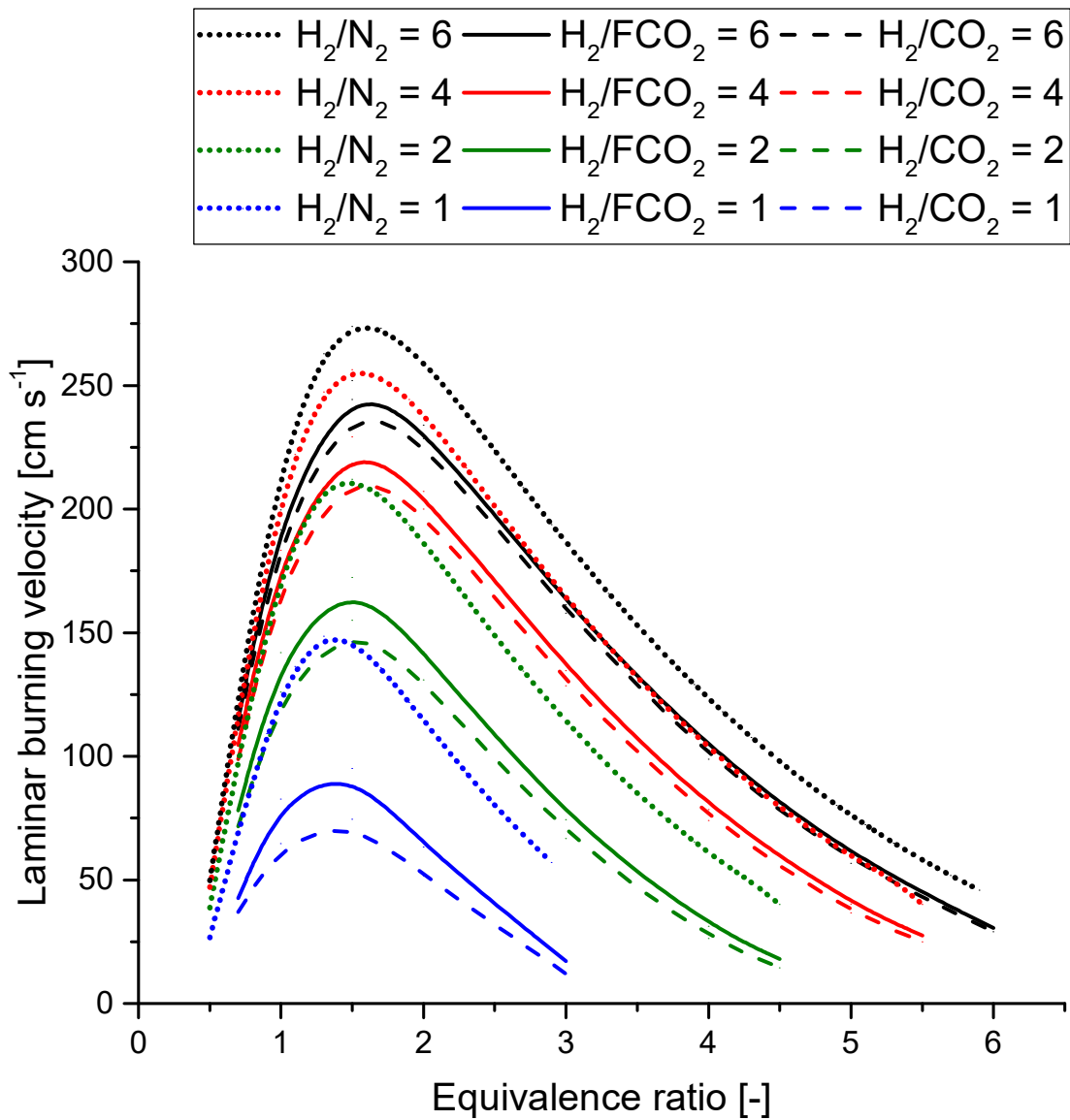
## 172 **Numerical results**

### 173 **Laminar Burning Velocity, Non-Stretched Flames**

174 The effects of the CO<sub>2</sub> share in the unburnt mixture on the laminar burning velocity estimated at  
175  $T_{\text{gas}} = 298$  K and  $p_{\text{gas}} = 1$  bar are reported in Figure 2 in dependence on the equivalence ratio. The case  
176 where N<sub>2</sub> was added to H<sub>2</sub> is included for comparison.

177





**Figure 2** Comparison of estimated LBV at 298 K and 1 bar, in dependence on the equivalence ratio (the notation X/Y stands for the volume ratio).

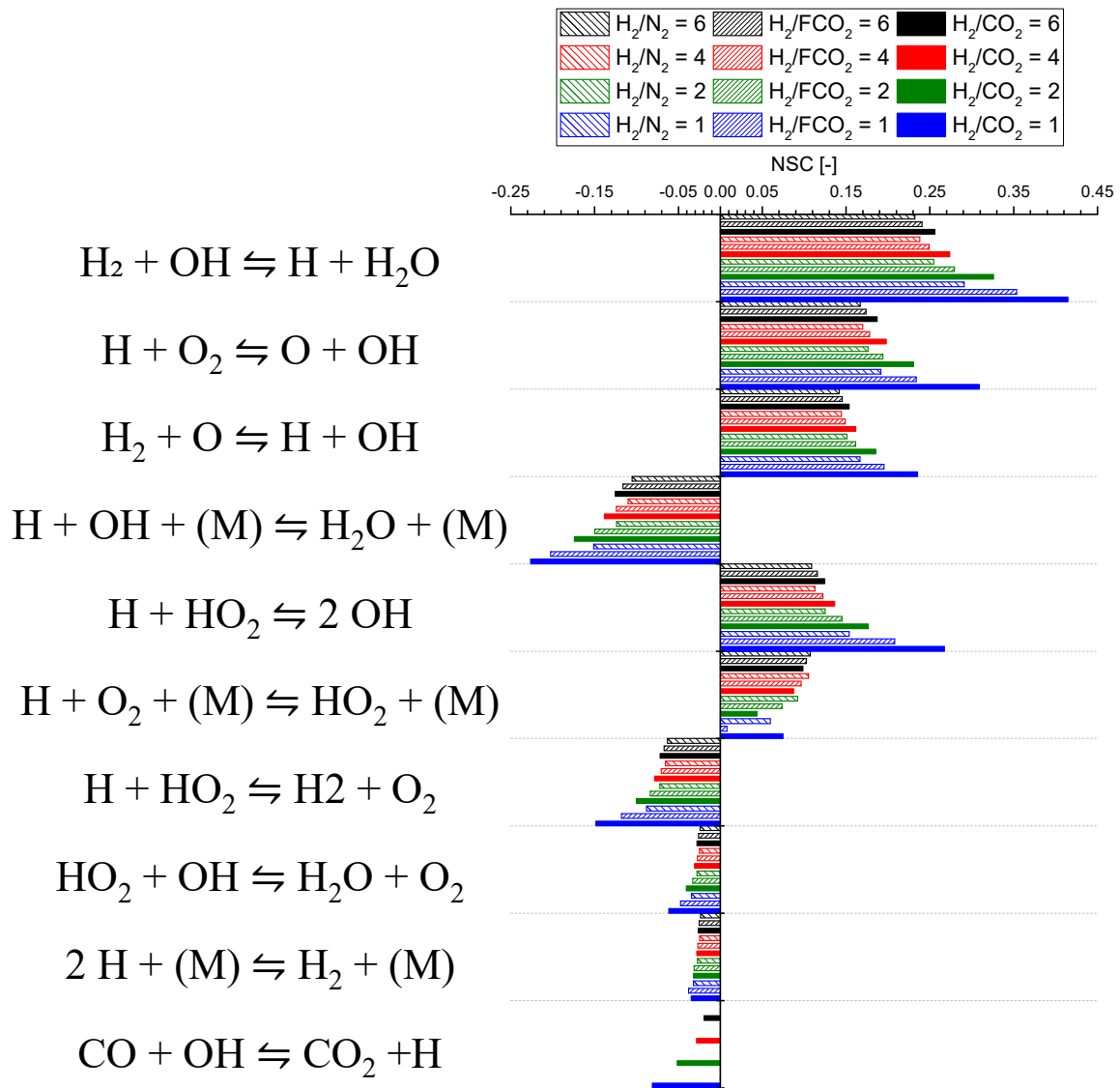
178

179 The introduction of FCO<sub>2</sub> has a significant effect regardless of the H<sub>2</sub>/CO<sub>2</sub> ratio increasing the  
 180 laminar burning velocity compared with CO<sub>2</sub>, especially at near-stoichiometric compositions. The  
 181 reduced overall burning velocity testifies to the chemical effects of CO<sub>2</sub>. FCO<sub>2</sub> can be viewed as  
 182 accounting for the thermal dilution only. The estimated laminar burning velocities of H<sub>2</sub>/FCO<sub>2</sub> and H<sub>2</sub>/N<sub>2</sub>  
 183 mixtures show significantly larger values for the second case, regardless of the equivalence ratio and  
 184 fuel composition considered. For example, the increase in the fundamental laminar burning velocity  
 185 achieves values up to 50% for elevated dilution (i.e., low H<sub>2</sub>/FCO<sub>2</sub> H<sub>2</sub>/N<sub>2</sub> ratios). This trend can be  
 186 explained considering the thermal inertia of the adopted diluents. It is worth noting that the observed

187 increase in the laminar burning velocity can be linearly associated with the variation of the average heat  
188 capacity ( $\bar{c}_p$ ), namely  $LBV_{H_2/N_2}/LBV_{H_2/FCO_2} \approx \bar{c}_{p_{H_2/N_2}}/\bar{c}_{p_{H_2/FCO_2}}$ . On the other hand, the magnitude of the  
189 effects of the chemistry of CO<sub>2</sub> on the LBV is largely influenced by the applied compositions. Indeed,  
190 the variation in the laminar burning velocity is limited to -10% for lean compositions, whereas it can  
191 reach ~-25% at stoichiometric and ~-40% in rich conditions. This trend is in line with the increased  
192 contribution of radicals in the conversion of the fuel typically attributed to the increase in equivalence  
193 ratios [39]. Considering the structure of the adopted mechanism, CO<sub>2</sub> plays either a direct role as a  
194 reactant/product dependent on the concentration or an indirect role as a diluent. The reaction associated  
195 with the formation of CO<sub>2</sub> via CO oxidation (i.e.,  $CO + OH \rightleftharpoons CO_2 + H$ ) is a clear example of the above-  
196 mentioned direct role. The presence of CO<sub>2</sub> alters the equilibrium, suppressing the formation of H  
197 radicals, thus potentially affecting the reactivity of the whole system. Conversely, reactions where CO<sub>2</sub>  
198 acts simply as inert diluent reducing the reaction rate by decreasing the reactant concentrations can be  
199 included into the group of indirect contributions.

200 For further clarification, the relevance of each reaction of the adopted mechanism was assessed  
201 through a sensitivity analysis. Although larger relative deviations between the dilution with FCO<sub>2</sub> and  
202 CO<sub>2</sub> are observed in rich compositions, the stoichiometric composition shows the largest absolute  
203 differences. Hence, the sensitivity analysis performed in this work was executed at 298 K, 1 bar, and  
204 stoichiometric composition (Figure 3) to assess the effect of CO<sub>2</sub> on the most influential reactions. For  
205 the sake of clarity, reactions are sorted by the absolute values of the NSCs and only the largest ten are  
206 listed.

207

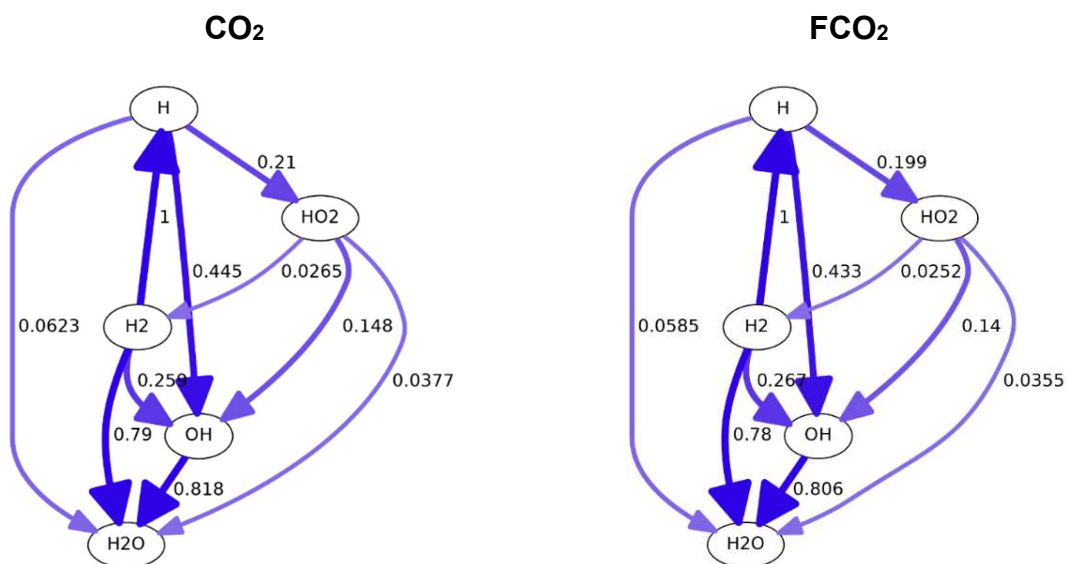


**Figure 3** Comparison of normalized sensitivity coefficients of the laminar burning velocity with respect to the rate constants at 298 K and 1 bar, as a function of the initial fuel composition at stoichiometric conditions (the notation X/Y stands for the volume ratio).

208

209 Regardless of the chemical and thermal properties of the diluent, increasing the H<sub>2</sub> content leads to a  
 210 general decrease in the absolute value of the NSCs. Besides, the comparison between the values for  
 211 the FCO<sub>2</sub> and N<sub>2</sub> dilution shows slightly lower values for the latter case, except for the H + O<sub>2</sub> + (M) ⇌  
 212 HO<sub>2</sub> + (M) reaction. This reaction represents the only case of a falloff reaction having CO<sub>2</sub> efficiencies  
 213 lower than that of H<sub>2</sub> among the ones reported in Figure 3. This observation suggests that the  
 214 competition between CO<sub>2</sub> (or FCO<sub>2</sub>) and H<sub>2</sub> has a detrimental effect on H + O<sub>2</sub> + (M) ⇌ HO<sub>2</sub> + (M).

215 Conversely, the direct role of CO<sub>2</sub> can be evaluated through the comparison between the CO<sub>2</sub> and FCO<sub>2</sub>  
 216 data. In most cases, larger NSCs are calculated for CO<sub>2</sub> dilution for a given fuel composition. These  
 217 trends imply that the presence of CO<sub>2</sub> makes the systems more sensitive to the chemistry of OH and H  
 218 radicals either from a kinetic or thermal point of view. It should be noted that the most influential reaction  
 219 directly involving CO<sub>2</sub> is CO + OH  $\rightleftharpoons$  CO<sub>2</sub> + H. NSCs corresponding to the FCO<sub>2</sub> and N<sub>2</sub> cases are  
 220 negligible for this reaction due to the inert character of these reactants. Hence, the presence of CO<sub>2</sub> can  
 221 promote the formation of CO and OH through the reverse reaction, consuming H. Besides, this reaction  
 222 offers the possibility to explain the differences in laminar burning velocities, as the NSC is negative and  
 223 the reaction is typical of near stoichiometric mixtures. These observations can be confirmed by the  
 224 reaction path analysis shown in Figure 4 for equimolar fuels (i.e., H<sub>2</sub>/CO<sub>2</sub> and H<sub>2</sub>/FCO<sub>2</sub> equal to 1) under  
 225 flame conditions, namely 1200 K, 1 bar, and stoichiometric mixture composition.  
 226



227 **Figure 4.** Reaction path analysis for CO<sub>2</sub> and FCO<sub>2</sub> in equimolar composition with H<sub>2</sub> and  
 228 stoichiometric conditions at initial temperature 1200 K and 1 bar.

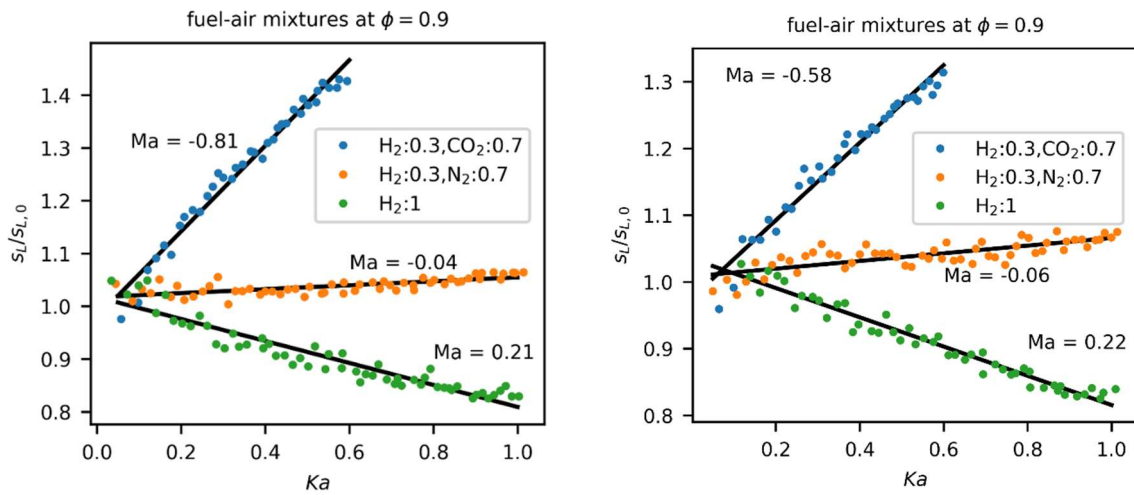
229 Although the general structure of the presented reaction paths is not affected by the fuel composition,  
 230 significant variations in branching ratios can be observed. The flux diagrams indicate that the presence  
 231 of CO<sub>2</sub> slightly affects the relative contribution of branches producing small radicals, except for the direct  
 232 production of H. Looking at the intermediates resulting from primary reactions involving H<sub>2</sub>, OH is  
 233 favoured by FCO<sub>2</sub> to the detriment of direct H<sub>2</sub>O formation. Combining these observations with the  
 234 results of the sensitivity analysis, it is obvious that CO<sub>2</sub> affects the competition between H<sub>2</sub> + O  $\rightleftharpoons$  H +

235 OH and  $\text{H}_2 + \text{O} + (\text{M}) \rightleftharpoons \text{H}_2\text{O} + (\text{M})$ . It should be noted that  $\text{CO}_2$  and  $\text{FCO}_2$  have the same collision  
236 efficiencies for any third body reaction included in the mechanism, leaving the reaction rate of  $\text{H}_2 + \text{O} +$   
237  $(\text{M}) \rightleftharpoons \text{H}_2\text{O} + (\text{M})$  unaffected. Therefore, the abovementioned differences can be mainly attributed to the  
238 difference in temperature due to the modified global heat release of the systems. The resulting excess  
239 in OH suppresses its production from H and  $\text{HO}_2$ , mostly attributable to  $\text{H} + \text{HO}_2 \rightleftharpoons 2 \text{OH}$ . Following the  
240 observations derived from the sensitivity analysis, the branch connecting H to OH is diminished by about  
241 3% at the investigated conditions through  $\text{FCO}_2$  with the chemical contribution from  $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 +$   
242 H.

243

#### 244 **Laminar Burning Velocity, Stretched Flames**

245 To investigate the effect of  $\text{CO}_2$  dilution on the burning velocity of stretched flames and possibly  
246 flame instabilities a one-dimensional counterflow flame is considered. The setup consists of two  
247 opposed nozzles with identical premixed hydrogen-dilutant-air mixtures at atmospheric conditions.  
248 Three cases at  $\phi = 0.9$  are considered, where the fuel consists of a) pure hydrogen, b) 30 mol-%  
249 hydrogen and 70 mol-%  $\text{CO}_2$ , and c) 30 mol-% hydrogen and 70 mol-% nitrogen. All cases are  
250 computed using the DRM19 reaction mechanism [40], which has been used in the literature for similar  
251 conditions, and the KiBO mechanism. Figure 5 shows the burning velocity over Karlovitz number, which  
252 represents the non-dimensional flame stretch (see equation 3) for the different fuel mixtures. The flame  
253 with pure hydrogen as a fuel has a positive Markstein number, which is indicative of a thermo-diffusively  
254 stable flame. The flame with nitrogen dilution has a Markstein number close to zero and is therefore  
255 insensitive to flame stretch. The flame with  $\text{CO}_2$  dilution on the other hand has a negative Markstein  
256 number.



257 **Figure 5** Burning velocity over Karlovitz number from the twin-counterflow flames for  
 258 different fuel mixtures and resulting Markstein numbers. Left: DRM19 reaction mechanism.  
 259 Right: KiBO reaction mechanism.

260

261 The reason for the negative Markstein number resulting from the CO<sub>2</sub> dilution is mainly attributed to  
 262 the reduction of the thermal diffusivity of the gas mixture and therewith the reduction of the Lewis  
 263 number. The thermal diffusivity of the fuel-oxidizer mixture with pure hydrogen at  $\phi = 0.9$  is  $a =$   
 264  $4.5 \times 10^{-5}$  m<sup>2</sup>/s, while the mixture thermal diffusivity with CO<sub>2</sub> dilution is  $a = 2.9 \times 10^{-5}$  m<sup>2</sup>/s. The  
 265 simulation with CO<sub>2</sub> dilution has been repeated by replacing CO<sub>2</sub> with the chemically inert FCO<sub>2</sub>.  
 266 Disabling the conversion of CO<sub>2</sub> leads to slightly higher burning velocities and a slightly larger Markstein  
 267 number ( $Ma = -1.0$ ), but otherwise the same trend is found. Likewise, changing the diffusion model  
 268 from the mixture-averaged model to the multi-component model including the Soret effect yields a similar  
 269 Markstein number of -0.99 for the H<sub>2</sub>-CO<sub>2</sub> mixture and +0.21 for the pure hydrogen flame (compare with  
 270 Tab. 2).

271 To validate these results, simulations of cases a) and b) have been repeated with the detailed GRI  
 272 3.0 reaction mechanism [41] and the reduced reaction mechanism by Kee [42]. For the pure hydrogen  
 273 flame, the reaction mechanisms by Li et al. [43], Konnov [44], and Connaire et al. [45] were included in  
 274 the comparison as well. While there are slight differences in the predicted burning velocity and Markstein  
 275 number, they all show the same tendency, i.e. a change from a flame with  $Ma > 0$  for pure hydrogen as  
 276 fuel to a flame with  $Ma < 0$  when considering dilution with CO<sub>2</sub>. The results are summarized in Table 2.  
 277 Flames with  $Ma < 0$  are potentially thermo-diffusively unstable. It should be noted that the GRI3.0

278 reaction mechanism has not been originally validated for methane-hydrogen blends and thus shows  
 279 considerable differences in flame speed compared with other reaction mechanisms, especially for case  
 280 b. Nonetheless, we included it here because GRI3.0 is still widely used today. Even though the  
 281 prediction of the laminar flame speed differs, the observed trend of CO<sub>2</sub> addition stays the same: the  
 282 Markstein number of the reactive mixture changes from positive to negative, showing that the addition  
 283 of CO<sub>2</sub> leads to a thermodiffusively unstable flame.

284  
 285

286 **Table 2** Burning velocity and Markstein number from the twin-counterflow flames obtained  
 287 with different reaction mechanisms at  $\phi = 0.9$

288

Case a (100 mol-% H <sub>2</sub> )			Case b (30 mol-% H <sub>2</sub> , 70 mol-% CO <sub>2</sub> )		
Mechanism	$s_{L,0}$ (m/s)	$Ma$	Mechanism	$s_{L,0}$ (m/s)	$Ma$
DRM19	2.24	+0.21	DRM19	0.111	-0.81
KiBO	2.12	+0.22	KiBO	0.107	-0.58
GRI3.0	2.02	+0.33	GRI3.0	0.066	-1.07
Kee	2.21	+0.32	Kee	0.138	-0.74
Li	2.02	+0.30			
Konnov	2.03	+0.33			
Connaire	1.97	+0.28			

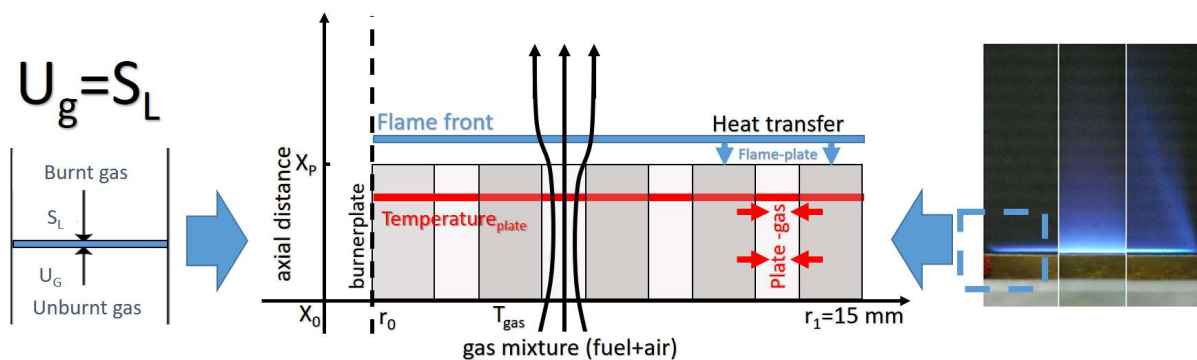
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290

## 291 Experiments for determining of the flame front instabilities

292 As stated above, flames with  $Ma < 0$  are potentially thermo-diffusively unstable. To investigate  
 293 thermo-diffusive instabilities and non-stable flame fronts, a flat flame burner with a stabilized flame was  
 294 selected also allowing optical examination of changes in the flame front over long examination intervals.  
 295 These burners are usually used to determine the laminar burning velocity of quasi-adiabatic flat flames.  
 296 The heat flux burner design used in the present work was proposed by de Goey et al. [46], based on  
 297 the fundamental experimental work done by [47]. The method has the advantage of directly measuring  
 298 the LBV of a planar stationary unstretched flame. The stabilization of a planar flame has been further

299 proved by [48] and can be achieved with a temperature-controlled burner plate compensating heat  
 300 losses from the flame. In the experimental setup used here the gas flow is controlled by three calibrated  
 301 mass flow controllers (MFCs). The ambient conditions as well as the signals from newly integrated type  
 302 T thermocouples are recorded and used to calculate the LBV [49]. By definition, the determination of  
 303 the laminar burning velocity is only possible for planar flames. Therefore, the radial temperature profiles  
 304 of the plate are analysed for up to 350 measurements to find conditions for adiabatic stabilisation of the  
 305 flame, i.e. the parabolic coefficient C of the radial temperature profile equals 0, see middle of figure 6.  
 306 For further details of the setup [50,51] and experimental uncertainties [52] related to gas flows and other  
 307 possible sources of errors, refer to Eckart et al. [53–56] and Rau et al. [57]. If instabilities and cellular  
 308 structures occur, a determination of the LBV is not permissible.

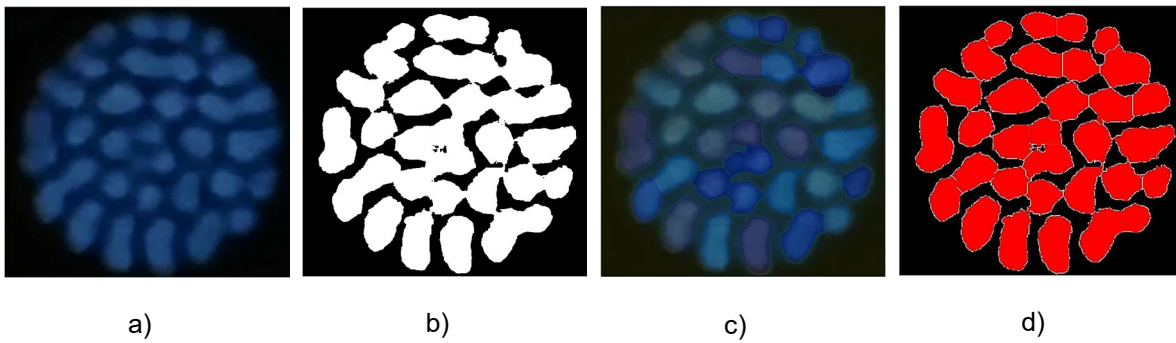


309 **Figure 6** Schematic drawing of the heat flux burner setup and the position of the stabilized  
 310 flame.

311 Experiments are conducted at equivalence ratios ( $\phi = 0.5\text{--}1.1$ ) and CO<sub>2</sub> contents up to 70% in  
 312 hydrogen. The initial gas temperatures are 300 K. Under these conditions, cellular structures could be  
 313 observed. To evaluate the behaviour of the flames and their instabilities, a VIS-camera was mounted  
 314 above the heat flux burner. With this optical setup, 10 pictures of the stabilized flame were taken at a  
 315 time interval of 120 s. These pictures were then evaluated carrying out a step binarization and reduction  
 316 of small interference effects due to reflections. Subsequently, edge detection and a watershed were  
 317 performed in a parameterized manner. This procedure made it possible to separate flame structures  
 318 from each other. The number of separated flames was evaluated and displayed graphically as an  
 319 overlay. The procedure can be seen step by step in Figure 7.

320



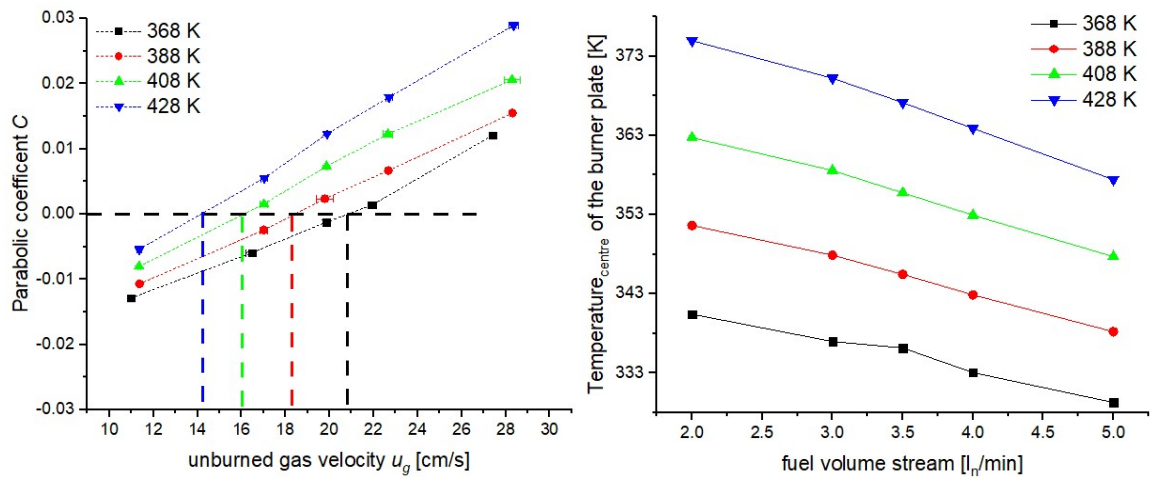


321 **Figure 7** Steps of image processing, a) raw data of the heat flux flame, b) binarization and  
 322 reduction of reflections, and c) overlay of detected watersheded cells and d) counting.

323

### 324 **Experimental results for flame structures**

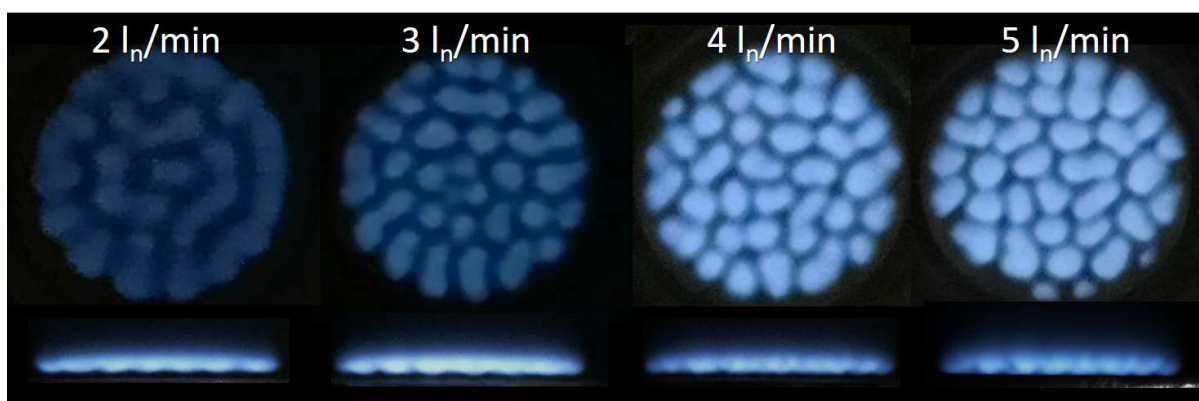
325 Experimental results obtained at atmospheric pressure for hydrogen-carbon dioxide-air mixtures at  
 326 various equivalence ratios of  $\phi = 0.5 - 1.1$  were analyzed. Figure 8 shows the comparison of measured  
 327 unburnt gas velocity and the parabolic coefficient  $C$  for equivalence ratio  $\phi = 0.9$  and a flame with 30 mol-  
 328 % hydrogen diluted by 70 mol-% of  $\text{CO}_2$ . In the experiments, different plate temperatures (368-428 K)  
 329 were applied. It was observed that the plate temperatures affect the parabolic coefficient, which is  
 330 normally used to interpolate to the adiabatic state. The overall trend of the results was not influenced by  
 331 the plate temperature. Since all the flames were not planar and therefore did not correspond to the  
 332 theoretical prerequisites for the determination of the laminar burning velocity, the inflow velocity cannot  
 333 be considered the same as the burning velocity even if the parabolic coefficient is  $C = 0$ . The  
 334 determination of the laminar adiabatic curvature and stretch free burning velocity was not possible for  
 335 the investigated regions, as impairments were detected in the flame in all cases. In the experiments, it  
 336 could be shown that with an increase in the velocity at the outlet and a corresponding increase in the  
 337 volumetric flow rate, the temperature in the middle of the plate decreased in the order of  $\Delta T_{\text{max}} \approx 15\text{K}$ .  
 338 These changes also had no influence on the flame shape of the  $\text{H}_2\text{-O}_2\text{-N}_2\text{-CO}_2$  flames.



**Figure 8** Measured parabolic coefficient and fuel volume stream as a function of plate temperature for a flame with 30 mol-% H<sub>2</sub> diluted by 70 mol-% of CO<sub>2</sub>, for equivalence ratio

$$\phi = 0.9 \text{ and } T_{\text{gas}} = 300 \text{ K}$$

339 In Figure 9 the flame morphology with view from above and from the side at the plate temperature of  
 340  $T_{\text{plate}} = 368 \text{ K}$  and varying flow rates are illustrated. The flames have been operated with 30 mol-%  
 341 hydrogen diluted by 70 mol-% of CO<sub>2</sub> at an equivalence ratio  $\phi = 0.9$  and  $T_{\text{gas}} = 300 \text{ K}$ . It can be seen  
 342 that the intensity of the individual flame structures increases significantly with inflow velocity. With  
 343 increasing inflow velocity, the flames are also stabilized further away from the burner plate and a  
 344 "sealed" flame front is no longer appearing. The change of this state can be seen in the range from 3 to  
 345 4 l<sub>n</sub>/min, whereby the transition from negative to positive parabolic coefficients can also be detected (see  
 346 Figure 8).

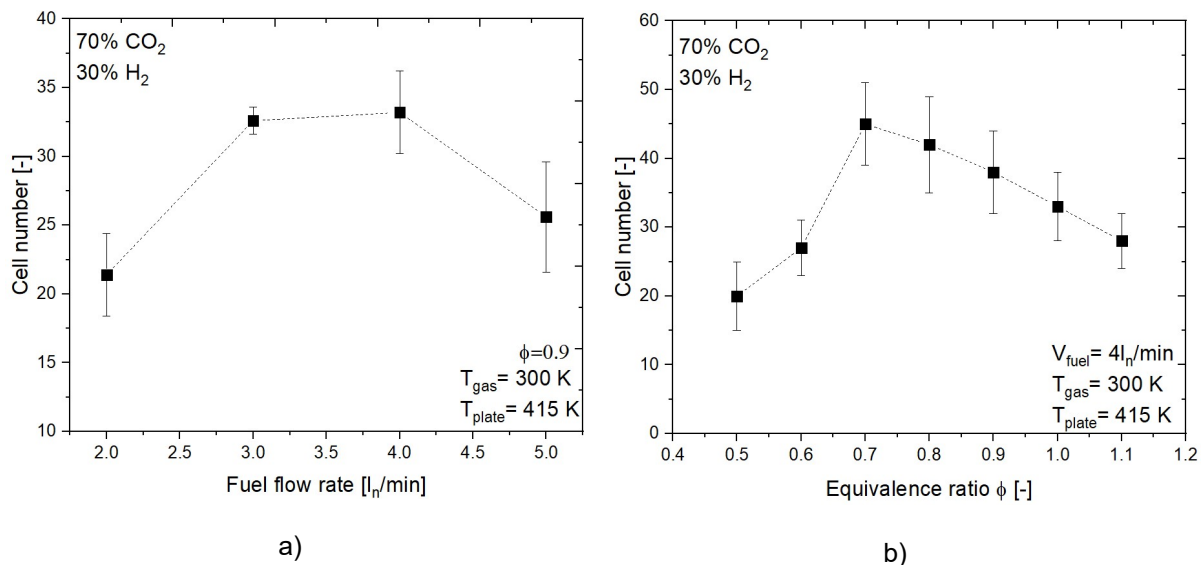


347 **Figure 9** Flame morphology for different volume streams with 30 mol-% hydrogen and  
 348 70 mol-% carbon dioxide for an equivalence ratio of  $\phi = 0.9$ ,  $T_{\text{gas}} = 300 \text{ K}$  and  $T_{\text{plate}} = 368 \text{ K}$ ,

349 top: top view, bottom: side view

350 For two different image series, one depending on the fuel flow and one on the equivalence ratio, the  
 351 number of cells in the broken flame front was analysed. The series were recorded independently of each  
 352 other. However, it can be seen that both overlap in the uncertainties regions. The maximum number of  
 353 cells is again located in the range of parabolic coefficients around  $C = 0$ . The number of cells is in the  
 354 same order of magnitude as found by Konnov et al. for methane flames, but below the ones of ethane  
 355 and propane flames. In this study, however, "closed" flame fronts were frequently found [25]. For the  
 356 highest volume flow rate tested, an evaluation of the number of individual cellular flames as a function  
 357 of the equivalence ratio was carried out according to the procedure described above. It turns out that a  
 358 maximum of around 45 cells could be found, as seen in Figure 10 b). Konnov et al. [25] could find the  
 359 maximum cell count for methane flames in the range of  $\phi = 0.8$ , whereas for ethane and propane higher  
 360 values were observed at  $\phi = 1.2-1.4$  and  $1.3$ , respectively.

361



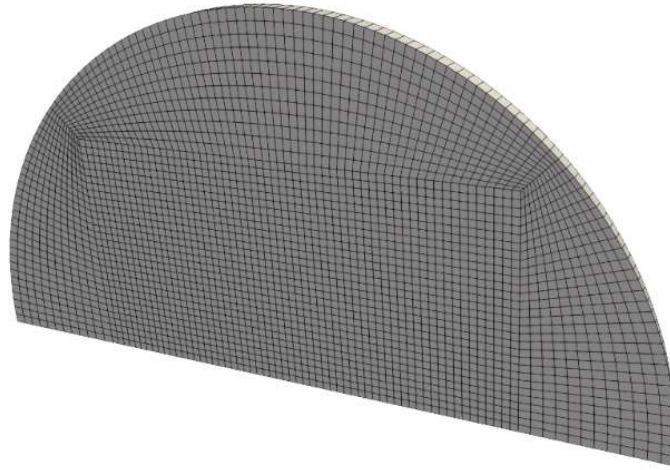
362 **Figure 10** Cell number a) depending on the fuel flow rate and b) the equivalence ratio

### 363 2-D Numerical Simulation of Spherically Expanding Flames

364 To investigate the thermo-diffusive instabilities caused by the CO<sub>2</sub> dilution further and to assess the  
 365 structure of the flames, detailed simulations of spherically expanding, constant pressure flames in  
 366 initially quiescent premixed fuel-air mixtures at atmospheric conditions ( $p = 1 \text{ atm}, T = 300 \text{ K}$ ) are  
 367 conducted. A H<sub>2</sub>-air (case a,  $\phi = 0.9$ , 100 % H<sub>2</sub>) and a H<sub>2</sub>/CO<sub>2</sub>-air flame from case b ( $\phi = 0.9$ , 30 mol-  
 368 % H<sub>2</sub> and 70 mol-% CO<sub>2</sub>) are simulated. The computational setup consists of a quasi-3D domain, which  
 369 is a wedge-shaped half-sphere, as shown in Figure 11. For the flame of case a, the diameter of the  
 370 computational domain is 16 cm and the mesh consists of 8.1 million finite volumes, yielding a resolution

371 in the equidistant region of the mesh of 33  $\mu\text{m}$ . For the  $\text{CO}_2$  diluted flame of case b, the diameter of the  
 372 domain is 48 cm and consists of 65 million finite volumes with a resolution of 56  $\mu\text{m}$ . The finer mesh for  
 373 the flame in case a is required due to the pure hydrogen flame having a lower flame thickness. Similarly,  
 374 the flame speed of the  $\text{CO}_2$  diluted flame is lower, and therefore a larger propagation distance is required  
 375 for the flame to develop the thermo-diffusive instabilities. In both cases, the flame zone is fully resolved  
 376 with more than 15 cells.

377



378 **Figure 11** Computational domain for the spherically expanding flames

379 The simulation is performed with an in-house solver for the detailed simulation of flames [58–60]  
 380 based on OpenFOAM [61] and Cantera, which has been validated in previous works [62–65]. It solves  
 381 the fully compressible Navier-Stokes equations together with a balance equation for energy and each  
 382 chemical species. The conservation of total mass reads

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0 \quad (4)$$

383  $\rho$  is the density,  $t$  time and  $\vec{u}$  is the gas velocity. The conservation of momentum is expressed as

$$\frac{\partial(\rho \vec{u})}{\partial t} + \nabla \cdot (\rho \vec{u} \vec{u}) = -\nabla p + \nabla \cdot \tau \quad (5)$$

384 with  $p$  the pressure and  $\tau$  the stress tensor

$$\tau = \mu \left( \nabla \vec{u} + \nabla \vec{u}^T - \frac{2}{3} \nabla \cdot \vec{u} \mathbf{I} \right) \quad (6)$$

385 and  $\mu$  being the dynamic viscosity of the reacting mixture.  $\mathbf{I}$  is the unit tensor. The balance of species  
 386 masses is expressed in terms of the mass fractions  $Y_k$  of species  $k$

$$\frac{\partial(\rho Y_k)}{\partial t} + \nabla \cdot (\rho \vec{u} Y_k) = \dot{\omega}_k - \nabla \cdot \vec{j}_k \quad (7)$$

387 where  $\dot{\omega}_k$  is the reaction rate of species  $k$  and  $\vec{j}_k$  its diffusive flux. Species diffusion is computed from a  
 388 mixture-averaged approach

$$\vec{j}_k = -\rho D_k \nabla Y_k \quad (8)$$

389 where  $D_k$  is the diffusion coefficient of species  $k$  computed from kinetic gas theory. The energy balance  
 390 is formulated in terms of the total sensible enthalpy:

$$\frac{\partial(\rho(h_s + \frac{1}{2}\vec{u} \cdot \vec{u}))}{\partial t} + \nabla \cdot (\rho \vec{u}(h_s + \frac{1}{2}\vec{u} \cdot \vec{u})) = -\nabla \cdot \vec{q} + \frac{\partial p}{\partial t} - \sum_k h_k^\circ \dot{\omega}_k \quad (9)$$

391  $h_k^\circ$  is the enthalpy of formation of species  $k$  and  $h_s$  the sensible enthalpy of the mixture.  $\vec{q}$  is the diffusive  
 392 heat flux

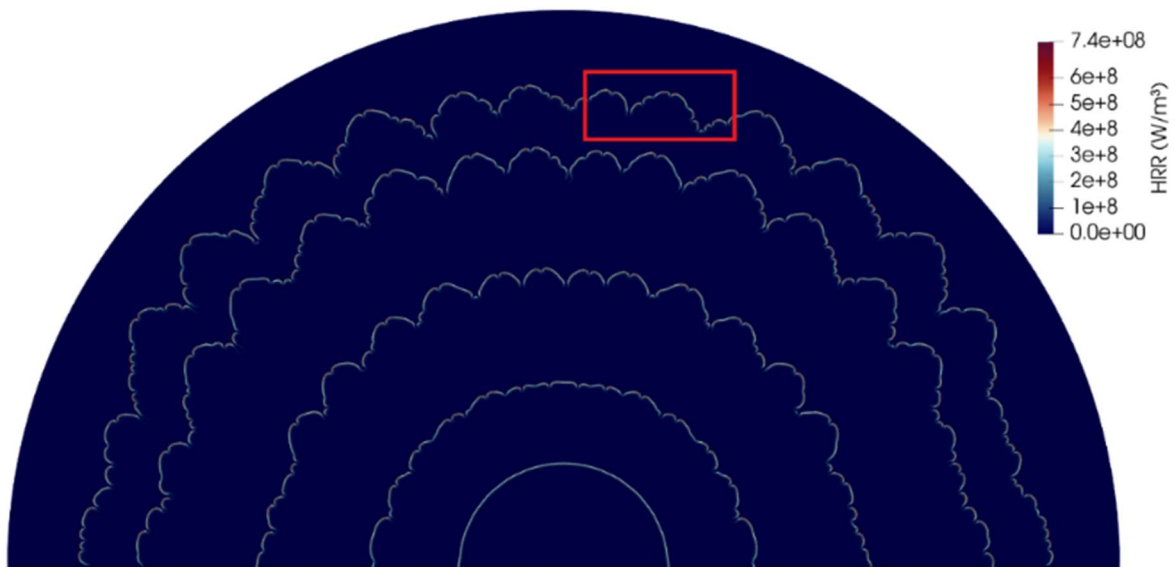
$$-\nabla \cdot \vec{q} = \nabla \cdot \lambda \nabla T - \sum_k \nabla \cdot h_{s,k} \vec{j}_k \quad (10)$$

393 where  $\lambda$  is the heat conductivity of the gas mixture,  $T$  is the temperature and  $h_{s,k}$  the sensible enthalpy  
 394 of species  $k$ .

395 The DRM19 reaction mechanism is used and chemical reaction rates are computed from finite rate  
 396 chemistry. The diffusion model is the mixture-averaged model. For time discretization, a second order  
 397 implicit method is used, while spatial discretizations are computed with fourth-order interpolation  
 398 schemes. The initial condition is given by a spherical flame kernel with a radius of 2 cm, obtained from  
 399 a one-dimensional pre-cursor simulation of a spherically expanding flame. The subsequent flame  
 400 propagation and development of instabilities is then captured during the simulation in detail.

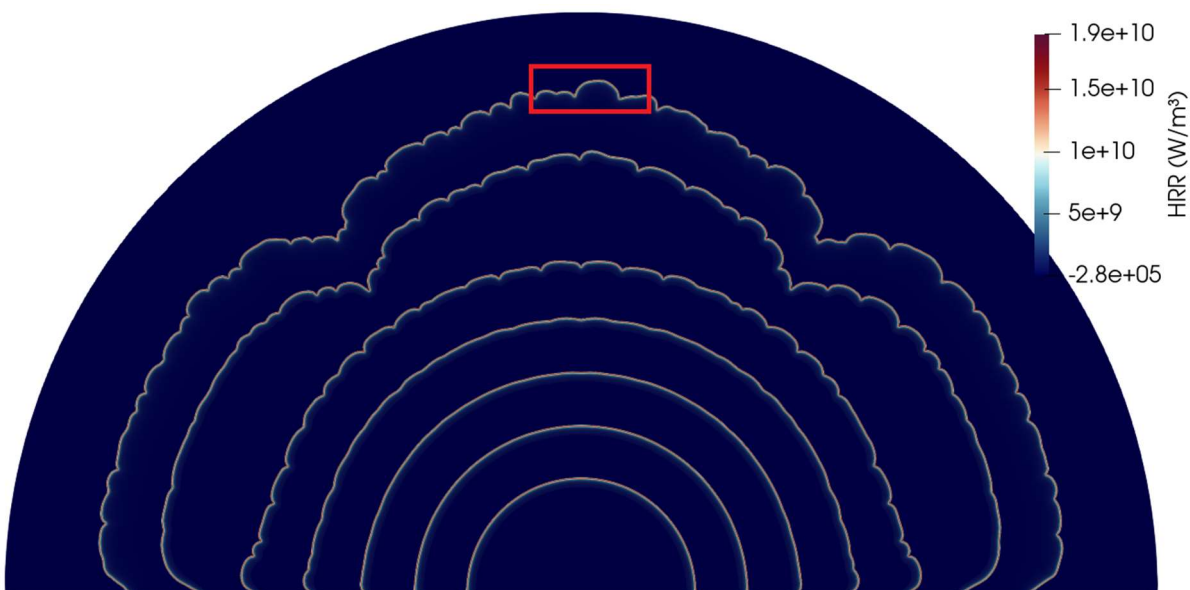
401 Figure 12 shows the temporal evolution of the flame front for the hydrogen-CO<sub>2</sub> fuel mixture of case b  
 402 during flame propagation in terms of the heat release rate (HRR) at different time instances. The flame  
 403 starts from a perfectly spherical configuration. While the flame expands, cellular structures form on the  
 404 flame front. The red box indicated in the top figure is later discussed in Figure 14.

405 At negatively curved parts of the flame front, the flame locally extinguishes, which is consistent with  
 406 the negative Markstein number. The structure of the cell formation follows the typical flame finger  
 407 configuration [66]. In this way, the H<sub>2</sub>-CO<sub>2</sub> flame at  $\phi = 0.9$  behaves the same as thermo-diffusively  
 408 unstable, lean ( $\phi \ll 1$ ) pure hydrogen flames [67].



409 **Figure 12** Flame front indicated by the heat release rate (HRR) at different time instances for  
 410 the flame from case b during spherical propagation.

411 Figure 13 shows the propagating pure hydrogen flame at  $\phi = 0.9$ , again in terms of heat release rate  
 412 at different time instances. As the flame reaches a sufficient radius, it becomes corrugated. However,  
 413 this corrugation is not an effect of thermo-diffusively unstable cellular structures, but a hydrodynamic  
 414 instability due to thermal expansion across the flame front (Darrieus-Landau instability), lacking the  
 415 typical structure of the flame fingers or thermo-diffusive cells. This distinction is shown more clearly in  
 416 Fig.14.

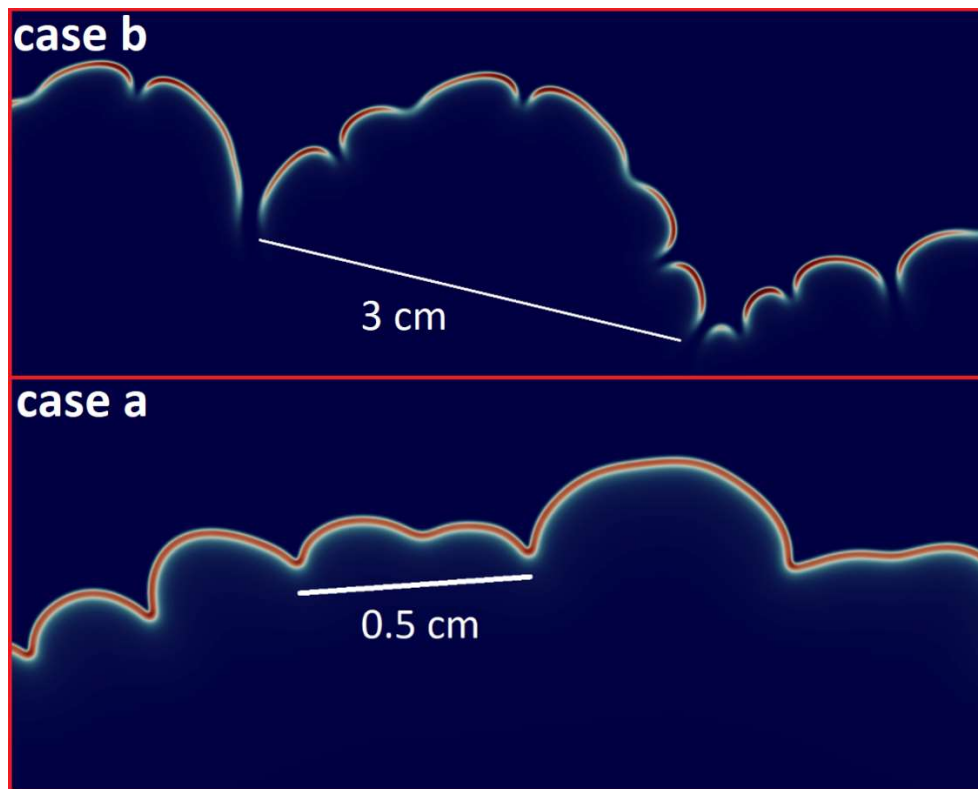


417 **Figure 13** Flame front indicated by the heat release rate (HRR) at different time instances for  
 418 the flame from case a during spherical propagation.

419

420 The reaction zones indicated by the red boxes from Fig. 12 and 13 are zoomed-in in Fig. 14. The top  
421 figure shows the CO<sub>2</sub> diluted flame. Due to the cellular structures caused by the thermo-diffusive  
422 instability, characteristic flame fingers develop [66]. These also have a characteristic length scale, in this  
423 case with a diameter of about 3 cm. The depicted heat release rate field also shows that the flame locally  
424 extinguishes at the negative curved parts of the flame front, and locally enhances at the positively curved  
425 parts of the flame front. This is in accordance with the negative Markstein number, as computed from  
426 the one-dimensional counterflow flame simulations. In this way, the H<sub>2</sub>-CO<sub>2</sub> flame at  $\phi = 0.9$  behaves  
427 the same as thermo-diffusively unstable, lean ( $\phi \ll 1$ ) pure hydrogen flames [67].

428 On the other hand, the zoom into the flame front of the pure hydrogen flame at  $\phi = 0.9$  does not  
429 show the typical cellular structure of thermo-diffusively unstable flames. Instead, the corrugations on the  
430 flame front are irregular, eventually forming cusps consistent with hydrodynamic instabilities. Again, in  
431 accordance with the low positive Markstein number from Table 2, the correlation of local heat release  
432 rate and flame curvature is reversed: in this case, the local heat release rate becomes maximal at the  
433 negatively curved parts of the flame front. Since the Markstein number is close to zero, the sensitivity of  
434 local flame speed or heat release rate with respect to flame curvature is low. Therefore, the variation of  
435 HRR along the flame front is low and no local extinction occurs.



436 **Figure 14** Zoomed-in regions from Fig. 12 and 13. Top: heat release rate field from the CO<sub>2</sub>  
 437 diluted flame from case *b*, showing the regular structure of the thermo-diffusively unstable  
 438 cells. Bottom: heat release rate field from the pure H<sub>2</sub> flame from case *a*, where the corrugation  
 439 results from a hydrodynamic instability with little variation of heat release rate along the flame  
 440 front.

441

## 442 **Conclusions**

443 In this paper premixed H<sub>2</sub>-CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> flames with air were investigated first numerically and the findings  
 444 have been afterwards confirmed in an experimental investigation. The utilization of a validated detailed  
 445 kinetic mechanism allowed for the evaluation of the effects of initial composition on the laminar burning  
 446 velocity, the most influential reactions, and the main oxidation paths of the investigated mixtures. The  
 447 relative contribution of thermal and chemical effects was quantified through the definition of a fictitious  
 448 CO<sub>2</sub> (FCO<sub>2</sub>), acting as an inert species having the same thermal and transport properties as CO<sub>2</sub>. The  
 449 obtained results showed that the presence of CO<sub>2</sub> strongly affects the chemistry of non-carbon  
 450 containing species because of the modifications in the reaction rate of  $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$ , potentially  
 451 causing significant differences in the ignition behaviour. Further, the effect of CO<sub>2</sub> addition in terms of



452 the flame structure has been investigated with two different numerical setups: the addition of CO<sub>2</sub> leads  
453 to a decrease in the mixture's thermal diffusivity and therewith a decrease in the Lewis number. This in  
454 turn changes the Markstein number for near-stoichiometric flames from slightly positive values for pure  
455 hydrogen flames to negative ones for H<sub>2</sub>-CO<sub>2</sub> flames. These results are independent of the employed  
456 reaction mechanisms and also if CO<sub>2</sub> is considered an inert species or not. Detailed simulation of a  
457 spherically expanding H<sub>2</sub>-CO<sub>2</sub> flame shows the expected cellular structures of thermo-diffusively  
458 unstable flames, which is not present for the pure hydrogen flame.

459 These results were verified by experiments using a heat flux burner. Adiabatic cellular flames of H<sub>2</sub>-CO<sub>2</sub>-  
460 O<sub>2</sub>-N<sub>2</sub> were identified visually and by photographic observations and the cellular structures have been  
461 quantified. Under specific experimental conditions, the flames become cellular; this led to significant  
462 modification of the flame propagation speed. Increasing the temperature of the burner plate up to  
463  $T_{\text{plate}} = 428 \text{ K}$  does not eliminate this instability for H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub>-CO<sub>2</sub> flames. Lowering the temperature of  
464 the burner plate extended the range of equivalence ratios over which cellularity was observed. No direct  
465 proportionality between the number of cells and inlet velocity in H<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub>-CO<sub>2</sub> flames was observed.  
466 Dependence of the number of cells as a function of equivalence ratio clearly showed a local maximum  
467 in the lean mixtures. In future studies, the influence of CO<sub>2</sub>/H<sub>2</sub> ratios as well as the influence of pressure  
468 and temperature on these instability phenomena will be investigated in more depth.

469

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474

475

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