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1 **Methane combustion in various regimes: First**
2 **and second thermodynamic-law comparison be-**
3 **tween air-firing and oxyfuel condition**

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17 **Abstract**

18 MILD oxyfuel combustion has been attracting increasing atten-
19 tion as a promising clean combustion technology. How to design
20 a pathway to reach MILD oxyfuel combustion regime and what
21 can provide a theoretical guide to design such a pathway are two
22 critical questions that need to be answered. So far there has been
23 no open literature on these issues. A type of combustion regime
24 classification map proposed in our previous work, based on the
25 so-called "Hot Diluted Diffusion Ignition" (HDDI) configuration,
26 is adopted here as a simple but useful tool to solve these problem-
27 s. Firstly, we analyze comprehensively the influences of various
28 dilution atmosphere and fuel type on combustion regimes. The
29 combustion regime classification maps are made out according to
30 the analyses. In succession, we conduct a comparison between the
31 map in air-firing condition and its oxyfuel counterpart. With the
32 aid of the second thermodynamic-law analysis on the maps, it is
33 easy to identify the major contributors to entropy generation in
34 various combustion regimes in advance, which is crucial for com-

35 bustion system optimization. Moreover, we find that, for the first
36 time, a combustion regime classification map also may be used as
37 a safety indicator. With the aid of these maps, some conclusions
38 in previous publications can be explained more straightforwardly.

39 **Keywords:**

40 MILD combustion; oxyfuel combustion; counter flow combustion;
41 entropy generation

42 **1 Introduction**

43 Although industrial and academic communities always pursue to
44 develop a more efficient way to generate heat and power, com-
45 bustion is still playing a predominant role in energy conversion of
46 most daily and industrial applications, not only in current stage
47 but also in the visible future [1]. Combustion usually faces two
48 main challenges: (1) to improve the efficiency of combustion pro-
49 cesses and (2) to reduce air pollutant products by combustion
50 processes. The former is extremely important for industries as it

51 contributes to their operational costs while the public pays high
52 attention on the latter as it concerns our well-being. Unfortunately,
53 ly, there is a tradeoff between these two respects as in general it
54 is difficult to eliminate air pollution while maintaining a high
55 combustion efficiency. To overcome this difficulty, some innova-
56 tive combustion technologies are inspired recently. Among them,
57 two, namely MILD (Moderate or Intense Low oxygen Dilution)
58 combustion [2] and oxyfuel combustion [3], attract increasing at-
59 tention.

60 Compared with the conventional combustion technologies, MILD
61 combustion is a type of "slow" reaction as the reactants are dilut-
62 ed to moderate the oxidization rates of fuels. Consequently, the
63 peak temperature of combustion will decrease and the tempera-
64 ture distribution will become even, which can eliminate thermal
65 NO_x production effectively [2]. Meanwhile, it was found that un-
66 burnt hydrocarbon products also could be reduced significantly
67 by MILD combustion [4]. It is an interesting feature as few avail-
68 able combustion technologies can satisfy, simultaneously, the re-

69 quirements of low NO_x emission and low unburnt hydrocarbon
70 production. More excitingly, it was observed that fuel nitrogen
71 translation also could be suppressed in MILD condition [5]. Due
72 to its intrinsic advantages, MILD combustion is regarded as a
73 promising clean combustion technology in this century [2]. Until
74 now, numerous research has been published on MILD combus-
75 tion. The majority of them may fall into five categories. The first
76 one tries to classify different combustion regimes by a map, which
77 can straightforwardly illustrate the relationship between various
78 combustion regimes. De Joannon et al. discussed how to classify
79 combustion regimes in a number of different combustion configu-
80 rations [6–8]. In their work the influences of various combustion
81 pressures were also investigated. In order to classify combustion
82 regimes more conveniently, some of the present authors[9] pro-
83 posed to adopt the effective equivalence ratio of reactants and
84 the temperature of oxidant flow as the coordinate axes, instead
85 of those used in Refs.[6,7], to plot the map, as these two parame-
86 ters can be obtained directly from practical combustion system-

87 s. The above studies all are based on the so-called counter-flow
88 combustion configuration. Recently, Wang et al. [10] investigated
89 the combustion regimes of a co-flow configuration. They observed
90 that in co-flow combustion there was a quasi-MILD regime which
91 was similar with MILD combustion but did not share the same
92 features of MILD combustion. More recently, Evans et al. [11]
93 proposed a new approach, based on the initial/final temperature
94 and the effective activation energy of reaction, to classify combus-
95 tion regimes. Their effort provided an insight into classification of
96 different types of combustion. The second category focuses on the
97 special reaction structures of MILD combustion. Szego et al. [12]
98 reported the profiles of temperature and concentration inside a
99 lab-scale furnace operated in MILD combustion condition. Their
100 work paid high attention on how to form MILD combustion sta-
101 bly. A so-called jet in hot coflow (JHC) burner was designed in
102 Ref.[13]. The temporally and spatially resolved measurements of
103 reactive scalars were carried out with the aid of this equipment.
104 As it can prevent atmosphere to affect the fine reaction structures

105 of MILD combustion within the core zone, the JHC burner has
106 been widely used in the MILD combustion research community,
107 especially for MILD combustion simulation. The influences of dif-
108 ferent fuels on reaction structures of MILD combustion also have
109 been reported [14,15]. It was found that MILD combustion was
110 highly flexible to various fuels. As MILD combustion is a kind of
111 "bulk" combustion, therefore the furnace chamber shape would
112 influence MILD combustion more significantly, as compared with
113 traditional combustion modes. Recently some of the present au-
114 thors discussed such topic[16]. The results demonstrated that a
115 larger divergence angle of a furnace would be better to estab-
116 lish MILD combustion. The publications on reaction structures
117 of MILD combustion are too many to be listed here. A detailed
118 review on it has been presented in Refs.[2,17]. The efforts on sim-
119 plified reaction mechanisms of MILD combustion constitute the
120 third category, which is indispensable for industrial-scale simu-
121 lation. Kim et al.[18] compared different global reaction mecha-
122 nisms for MILD combustion simulation. As their study was based

123 on the so-called "Sandia Flame-D" which is not a typical MILD
124 combustion research prototype, the conclusions drawn in Ref.[18]
125 were questionable. Some of the present authors also made an
126 comprehensive comparison between several popularly used glob-
127 al reaction mechanisms, with the aid of the JHC configuration
128 [19]. It was observed that these global reaction mechanisms all
129 could predict the major concentrations sufficiently accurately, ex-
130 cept carbon monoxide. Based on the analyses, the same authors
131 proposed a new global reaction mechanism for MILD combus-
132 tion research [20]. Compared against the GRI-Mech3.0, Hamdi
133 et al.[21] proposed a 5-step and a 9-step reduced reaction mecha-
134 nism for natural gas MILD combustion simulation. They claimed
135 that the latter was better for NO_x and CO prediction. Nitro-
136 gen translation pathways in MILD combustion condition were
137 also investigated[22–26]. Some studies revealed that the NNH and
138 N_2O routes were the most important pathways in NO formation
139 in MILD condition [27–31]. The next category covers the aero-
140 dynamics of MILD combustion. Historically, MILD combustion

141 can be looked as a variant of High Temperature Air Combustion
142 (HiTAC)[2]. Consequently, in the early stage of MILD combus-
143 tion research, preheating of reactants was regarded as one of the
144 necessary conditions to establish MILD combustion. Later, it was
145 found that aerodynamics played a predominant role on sustain-
146 ing MILD combustion and a MILD regime might be formed in
147 a furnace even without preheating [32]. In succession, it was re-
148 ported, compared with traditional combustion modes, molecular
149 diffusion could not be ignored in the MILD combustion regime
150 investigated in Ref.[33]. The latest research concentrates in the
151 effect of aerodynamics on reaction rates of fuels in MILD regime,
152 namely the so-called turbulence-chemistry interaction [34,35], as
153 it has been widely accepted that most popularly used models
154 for turbulence-chemistry interaction were not suitable for MILD
155 combustion simulation [9]. The above research all are based on
156 the first thermodynamic-law analysis. Recently, a number of stud-
157 ies starting from the second thermodynamic-law begin to emerge.
158 In this paper they are classified as the last category. In Ref.[36]

159 it was revealed that the exergy efficiency of a lab-scale furnace
160 operated in MILD combustion regime is significantly higher than
161 that under conventional combustion conditions. The same au-
162 thors showed this conclusion could hold water for different fu-
163 els[37]. A comparison of entropy generation between different
164 combustion regimes was made by the present authors [9]. It was
165 observed that the maximum exergy loss in hydrogen-air MILD
166 combustion regime depended closely on a number of operational
167 parameters.

168 At first, the oxyfuel combustion technology was developed to ad-
169 dress the global warming challenge due to the intensive man-
170 made CO₂ emissions[3,38]. Soon, it was observed that some air
171 pollutant products also could be suppressed in oxyfuel condi-
172 tion [39]. Numerous studies have been published during the past
173 decades on different aspects of oxyfuel combustion, such as burn-
174 er design [40,41], reaction mechanisms [42,43], techno-economic
175 assessment[44,45] and so on. A number of review papers are also
176 available[39,46,47]. A latest review on numerical modeling of oxy-

177 fuel combustion is presented in Ref.[48]. The oxyfuel combustion
178 technology is regarded as one of the most promising options in the
179 near future to restrict CO₂ concentration in the atmosphere [3].
180 Until now, some pilot-scale demonstrations have been built up
181 and a number of commercial-scale units are under consideration
182 [49].

183 To remedy some shortcomings of the "standard" oxyfuel com-
184 bustion technology, recently a so-called MILD oxyfuel conception
185 was proposed [20,50–53]. The MILD oxyfuel combustion is an or-
186 ganic combination of MILD and oxyfuel technologies, namely to
187 establish and sustain a MILD combustion regime in CO₂/O₂ at-
188 mosphere [20]. Originally, the present authors proposed this new
189 conception to utilize biogas with a higher efficiency[20,51]. Later,
190 it was extended to different fuels [50,52,53]. The fine structures of
191 MILD oxyfuel combustion have been investigated with the aid of
192 numerical simulation [20,51–53] and its feasibility has also been
193 proven by experimental studies [50]. However, as a recently e-
194 merging research area, a lot of efforts are still required to deepen

195 our insight into it. For example, from the viewpoint of industrial
196 practice, it is impossible to reach a MILD oxyfuel regime direct-
197 ly. According to our experimental experience, a safe pathway to
198 establish and sustain a MILD oxyfuel regime in a furnace may
199 be: air-firing \rightarrow oxyfuel combustion \rightarrow MILD oxyfuel regime [54].
200 However, how to design a safe and effective transition pathway is
201 still an open question. More important, we should answer what
202 can be used as a theoretical guide to design such a transition
203 pathway for practical applications. Unfortunately until now no-
204 body has focused on these critical problems. After a careful con-
205 sideration, a type of map on combustion regime classification,
206 which was proposed in our recent investigation [9], may provide
207 an appropriate option to solve these problems. Therefore, maps to
208 classify various combustion regimes in air-firing and oxyfuel con-
209 dition, besides a comparison between these maps, are extremely
210 necessary. With such combustion regime classification maps and
211 related comparison, we may further optimize the transition path-
212 ways for practical operation in advance. But surprisingly, to the

213 best knowledge of the present authors, nowadays there is no open
214 literature on it. As mentioned above, until now there have been
215 only a number of studies on combustion regime classification in
216 air-firing condition. Such gap inspires the present work.

217 The main originalities of the present work is fourfold: (1) For
218 the first time, we analyze comprehensively the influences of dif-
219 ferent dilution atmosphere on combustion regimes. According to
220 the analyses, the combustion regime classification maps are made
221 out. (2) In succession we make a comparison between the map
222 in air-firing condition and its oxyfuel counterpart, not only from
223 the viewpoint of the first thermodynamic-law but also from that
224 of the second thermodynamic-law. The comparison provides a
225 consistent solution to the above problems with a solid theoretical
226 base. (3) With the aid of the second thermodynamic-law analysis
227 on the maps, it is easy to identify the major contributors to en-
228 tropy generation in various combustion regimes in advance, which
229 is crucial for combustion system optimization. (4) Through the
230 comparison between different fuels, we find that, for the first time,

231 a combustion regime classification map can be used as a safety
232 indicator for practical operation. Such exciting finding can exten-
233 sively expand the purposes of a combustion regime classification
234 map. Moreover, with the aid of these maps, some conclusions
235 in previous publications can be explained more straightforward-
236 ly. Meanwhile, a new question is arisen: whether the conclusions
237 in the present work can be extended for other fuels. It will be
238 answered by our future work.

239 **2 Specification of the problem and mathematical modeling**

240 The so-called "Hot Diluted Diffusion Ignition" (HDDI) configu-
241 ration is adopted in the present work as it is a popularly used
242 research prototype to classify combustion regimes [7]. Such con-
243 figuration is composed by two opposed jets: one jet for oxidant
244 flow and the other for fuel flow, as illustrated by Fig.1. The as-
245 pect ratio of the investigated domain is $A = \frac{L}{W} = 0.6$, where W
246 is the diameter of jets and the distance between the jets is $2L$. In
247 this figure, the boundary conditions are also given, the same as

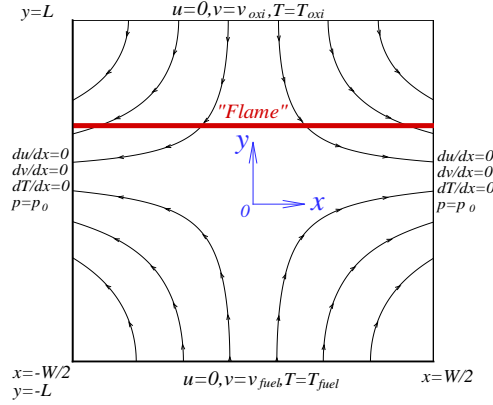


Fig. 1. Schematic configuration and coordinate system of the computational domain adopted in our previous work [9,20,51].

248 that in our previous work [9,20,51]. Two-dimensional rectangular
 249 coordinates are used. The origin of the coordinates is located at
 250 the domain geometric center. Fuel flow (CH_4/CO_2 in oxyfuel op-
 251 eration and CH_4/N_2 in air-firing operation), is uniformly ejected
 252 from the bottom wall with velocity $v = v_{fuel}$ and temperature
 253 $T_{fuel} = T_0$, where T_0 is the atmosphere temperature. The pre-
 254 heated oxygen (diluted by CO_2 in oxyfuel operation and N_2 in
 255 air-firing operation), is uniformly ejected from the top wall with
 256 velocity $v = v_{oxi}$ and temperature T_{oxi} . The counter flow impact-
 257 s and reacts in the reaction zone. Then, a diffusion stagnation
 258 "flame" is formed.

259 The dimensionless governing equations in Cartesian coordinates

260 for such laminar steady reacting flows have been given in our
 261 previous studies [51], which read

$$262 \quad \partial_t \rho + \nabla_\alpha \rho u_\alpha = 0, \quad (1)$$

$$263 \quad \partial_t \rho u_\alpha + \nabla_\beta \rho u_\alpha u_\beta = -\nabla_\alpha P + \frac{1}{Re} \nabla_\beta \mu (\nabla_\alpha u_\beta + \nabla_\beta u_\alpha), \quad (2)$$

$$264 \quad \partial_t T + u_\alpha \nabla_\alpha T = \frac{1}{\rho Re Pr} \nabla_\alpha \mu \nabla_\alpha T + \sum_{i=1}^N h_i \omega_i, \quad (3)$$

$$265 \quad \partial_t Y_i + u_\alpha \nabla_\alpha Y_i = \frac{1}{\rho Re Sc} \nabla_\alpha \mu \nabla_\alpha Y_i + \omega_i, \quad (4)$$

$$266 \quad \rho = \frac{\bar{W}}{RT}. \quad (5)$$

267 where $Re = \rho_0 u_0 L_0 / \mu_0$, $Pr = \mu Cp / (\rho \kappa)$ and $Sc = \mu / (\rho D_i)$ are
 268 the Reynolds, Prandtl and Schmidt numbers respectively. The
 269 variables, such as density ρ , velocity u_α , temperature T and total
 270 pressure P , are normalized by the reference values of density ρ_0 ,
 271 velocity u_0 , temperature T_0 , length L_0 , static pressure p_0 and dy-
 272 namic viscosity μ_0 . The detailed normalized process can be found
 273 in [20,51]. \bar{W} is the mean molecular weight of the mixture and
 274 Cp is the specific heat capacity of the reactants[55]. The above
 275 governing equations are derived under the low Mach number as-

280 sumption together with the following premises: (1) There are no
281 external forces; (2) The diffusion obeys the Fick's law of diffu-
282 sion; (3) Viscous energy dissipation is neglected. The subscripts
283 α and β in the above equations represent Cartesian coordinates
284 and the summation convention is applied to these subscripts. The
285 heat inter-diffusion term does not appear in the above equations
286 because the terms of second order and above in the Mach number
287 have been neglected under the low Mach number approximation
288 [55].

289 The inlet Reynolds number is defined as[51]

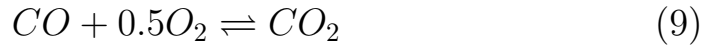
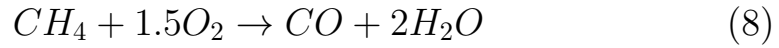
$$290 \quad Re = \frac{v_{air}L}{\nu_{air}}, \quad (6)$$

291 where ν_{air} is the kinematic viscosity of air. The velocity v_{fuel} is
292 determined by

$$293 \quad Re = \frac{v_{fuel}L}{\nu_{fuel}}, \quad (7)$$

294 where ν_{fuel} is the kinematic viscosity of fuel mixture and $2L$ is
295 the distance between the opposed jets. In the present work, the

296 Reynolds numbers of both jet flow are identical as $Re = 100$
 297 and a simple lattice Boltzmann approach proposed in our previ-
 298 ous research [55] is used to solve the above governing equations.
 299 The thermodynamic and transport properties appearing in the
 300 governing equations are given in our previous work [43]. The re-
 301 action kinetic mechanisms used in our previous studies [43,20]
 302 are adopted here again, as shown below:



$$\omega_{ov} = k_{ov} T^\beta \prod_{j=1}^N \left(\frac{\rho Y_j}{W_j} \right)^{\alpha_j} \exp(-E/RT) \quad (11)$$

303 where β is the temperature exponent, ω_{ov} is the over-all reaction

Table 1

Global combustion mechanisms with kinetic rate data (unit in kmol, m^3 , K, s, KJ).

Reaction mechanism	Rate orders	β	k_{ov}	E/R
(R1) $CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$	$[CH_4]^{0.7}[O_2]^{0.8}$	0	5.03×10^{11}	24056
(R2) $CO + 0.5O_2 \rightarrow CO_2$	$[CO][H_2O]^{0.5}[O_2]^{0.25}$	0	2.24×10^8	5032
(R3) $CO_2 \rightarrow CO + 0.5O_2$	$[CO_2][H_2O]^{0.5}[O_2]^{-0.25}$	-0.97	1.10×10^{13}	39452
(R4) $H_2O \rightarrow H_2 + 0.5O_2$	$[H_2O]$	0	3.48×10^{13}	47907
(R5) $H_2 + 0.5O_2 \rightarrow H_2O$	$[H_2][O_2]^{0.5}$	0	7.91×10^{10}	17609

304 rate, k_{ov} is the reaction coefficient, E is the effective activation
305 energy, R is the universal gas constant and α_j , Y_j and W_j are the
306 reaction exponent, mass fraction and molecular weight of the j -
307 th reactant. The corresponding reaction rate data in these global
308 chemical reaction mechanisms are given in Table 1.

309 3 The entropy generation equation

310 As mentioned above, the flow field and the distribution of scalar
311 properties, such as temperature and species mass fractions, are
312 obtained from numerical solution of the above governing equa-
313 tions. From the flow and scalar field distributions, the local en-
314 tropy generation number can be computed using the entropy gen-

315 eration equation, which is obtained in the following form[51]:

$$316 \quad S = \frac{\Pi : \nabla \vec{u}}{T} + \frac{k \nabla T \cdot \nabla T}{T^2} + \sum_i \frac{\rho D_i}{x_i} \nabla y_i \cdot \nabla x_i - \sum_i \frac{\mu_i \omega_i}{T} \quad (12)$$

317 What should be accentuated is that Eq.(12) adopted in the present
318 work is also dimensionless. The first term on the right-hand side
319 of Eq. (12) is due to fluid friction (referred to as S_{vis}), the second
320 term is due to heat transfer (referred to as S_{cond}), the third ter-
321 m pertains to mass transfer (referred to as S_{mix}) and the fourth
322 term is due to chemical reaction (referred to as S_{chem}). The last
323 two terms have summation over all the species and for all the
324 reactions. Because there is no external body force in the present
325 situation, the entropy generation induced by body force vanishes
326 in Eq. (12). The entropy generation term due to coupling between
327 heat and mass transfer also can be ignored in the above equation
328 since it usually makes rare contribution to the local entropy gen-
329 eration rate unless the Soret and Dufour effects have significant
330 influence[56]. In Eq. (12), Π is the viscous stress, \vec{u} is the veloc-
331 ity vector, ρ is the density of the mixture and k is the thermal

332 conductivity. y_i , x_i , ω_i , D_i and μ_i are the mass fraction, the mole
 333 fraction, the production rate, diffusion coefficient and chemical
 334 potential of species i respectively. The total entropy generation
 335 number is defined as[51]

$$336 \quad S_{total} = \int_{\Omega} S \partial \Omega \quad (13)$$

337 where Ω means the global computational domain. Similar expres-
 338 sions can be written for $S_{vis,total}$, $S_{cond,total}$, $S_{mix,total}$ and $S_{chem,total}$.

339 The relative total entropy generation rates due to heat trans-
 340 fer, chemical reaction, fluid friction and mixing are defined as

$$341 \quad \gamma_{cond,total} = S_{cond,total}/S_{total}, \gamma_{chem,total} = S_{chem,total}/S_{total}, \gamma_{vis,total} =$$

$$342 \quad S_{vis,total}/S_{total} \text{ and } \gamma_{mix,total} = S_{mix,total}/S_{total} \text{ [56].}$$

343 4 Results and discussions

344 The grid resolution used in this work is 300×180 . It has been
 345 demonstrated in our previous studies [9,20,51] that such grid res-
 346 olution is fine enough for the present investigated domain. The

347 validation of our computer programme code has been presented
348 in detail in our previous publications [9,20,51,55,56]. The equiva-
349 lence ratio φ and the temperature of oxidant flow T_{oxi} are adopted
350 here as the arguments to classify different combustion regimes.
351 As demonstrated in our previous work [9], these two parameter-
352 s can be available straightforwardly in practical applications. In
353 the present investigation, the variable range of φ is very wide,
354 from the highly diluted fuel region ($\varphi < 0.5$) to the fuel-rich re-
355 gion ($\varphi = 1.4$) and T_{oxi}/T_0 varies from 1.0 to 6.0. What should
356 be emphasized is that for $T_{oxi}/T_0 = 1.0$, a temporary high tem-
357 perature source is required to ignite the reactants, the same as
358 that in our previous studies [20,55].

359 *4.1 Influences of fuel type and dilution atmosphere on combustion regimes*

360 In this subsection, the influences of different fuels and dilution
361 atmosphere on combustion regimes are discussed. The influences
362 of fuels on combustion regimes are revealed through a compari-
363 son between methane and hydrogen in air-firing condition while

364 methane HDDI combustion in air and CO₂/O₂ (oxyfuel) atmo-
365 sphere are chosen to show the influences of dilution atmosphere
366 on combustion regimes.

367 *4.1.1 Temperature profiles in air-firing condition and comparison between*
368 *different fuels*

369 Figure 2 illustrates the temperature profiles of methane-air HD-
370 DI combustion at various equivalence ratio and preheating tem-
371 perature of oxidant flow, where $\varphi = 0.5$ (critical point of ultra-
372 lean/highly diluted fuel region), $\varphi = 0.7$ (critical point of ultra-
373 lean/lean fuel region), $\varphi = 1$ (stoichiometric reaction) and $\varphi =$
374 1.1 (fuel-rich region) are chosen as the representatives for the
375 cases investigated in the present work. As shown by this fig-
376 ure, in air-firing condition, without preheating, reaction can not
377 take place in the highly diluted and ultra-lean fuel region (i.e.
378 $\varphi \leq 0.7$). Through our simulation, $\varphi = 0.793$ is the minimum
379 for the methane-air HDDI configuration to trigger reaction with-
380 out preheating (as shown by Fig. 2(a), when $T_{oxi}/T_0 = 1.0$ and
381 $\varphi \leq 0.7$ there is no temperature rise). With a relatively low pre-

382 heating temperature (namely, $T_{oxi}/T_0 = 2.0$), combustion can be
383 sustained stably in the fuel lean region. With a higher preheat-
384 ing temperature, such as $T_{oxi}/T_0 = 3.0$, stable reaction can occur
385 even in the highly diluted region as the preheating temperature
386 now is above the ignition temperature of methane. For some pre-
387 heating temperatures, such as $T_{oxi}/T_0 = 3.0$ and 4.0 , there will be
388 an obvious peak in the temperature profile even when $\varphi = 0.5$,
389 which implies with a high preheating temperature the heat re-
390 leased in the highly diluted fuel region also can generate a local
391 "hotspot" and it is harmful to establish an even temperature
392 distribution. With a much higher preheating temperature (e.g.
393 $T_{oxi}/T_0 \geq 5.0$), such negative influence on forming even tem-
394 perature distribution can be suppressed. In air-firing condition,
395 the maximum temperature in the fuel-rich region is substantial-
396 ly higher than its fuel-lean counterpart. Consequently, if a fuel-
397 rich scenario appears in practical operation, the fluctuation of
398 fuel flow should be paid high attention to avoid potential safety
399 problems.

400 In our previous study [9], we investigated hydrogen-air combus-
401 tion in various regimes. A comparison between Fig.2 in this work
402 and Fig. 2 in Ref.[9] indicates the composition of fuels will influ-
403 ence reaction structures significantly. As shown in Ref.[9], the re-
404 action zone of hydrogen-air HDDI combustion will become thick
405 obviously and will expand to the oxidant jet side with T_{oxi} and φ
406 increasing. However, different from its hydrogen counterpart, the
407 thickness of the reaction zone of methane-air HDDI combustion
408 is nearly insensitive to T_{oxi} and φ . Such observation is impor-
409 tant for burner design, especially for some demonstration-scale
410 furnaces in which opposed burners were equipped[54]. This dif-
411 ference may result from that the diffusivity of methane is much
412 smaller than hydrogen. Meanwhile, there are some similarities
413 between methane-air HDDI combustion and its hydrogen coun-
414 terpart. In hydrogen-air HDDI combustion, it was observed no
415 matter whatever T_{oxi} was, the maximum temperature of reac-
416 tants (T_{max}) increased with φ but the increment of T_{max} decreased
417 against T_{oxi} [9]. This conclusion is true for its methane counter-

418 part. As illustrated by Fig.2, T_{max} climbs up with φ and the in-
 419 creasing rate of T_{max} becomes slow against T_{oxi} . It can be shown
 420 more clearly from Fig. 3. Moreover, according to Fig. 3, it can
 421 be observed that for $\varphi \leq 1.0$, T_{max} will grow up almost linearly
 422 with T_{oxi} if the reactants can be ignited. In the fuel lean region
 423 ($0.7 \leq \varphi < 1.0$), the lines are nearly parallel with each other.
 424 While in the ultra-lean and highly diluted fuel region ($\varphi < 0.7$)
 425 the lines will intersect at $T_{oxi} = 6.0$. Such observation indicates,
 426 with a high preheating temperature, if fuel supply is not sufficien-
 427 t, the heat released by the exothermic reactions is much smaller
 428 than the energy borne by the preheated oxidant flow. Especial-
 429 ly in the highly diluted fuel region ($\varphi \leq 0.5$), the heat released
 430 by the exothermic reactions may not compensate heat loss, as
 431 depicted by Fig.2 (f): where a temperature peak appears when
 432 $\varphi = 0.7$, there is a temperature drop for $\varphi = 0.5$. This phe-
 433 nomenon does not exist when $T_{oxi} \leq 5.0$ (except the cases with
 434 $T_{oxi} \leq 2.0$ as in which reactions are not triggered). $T_{oxi} = 5.0$
 435 perhaps is a critical temperature point for the cases investigated

436 in the present work as at this preheating temperature level there
437 is no temperature rise or temperature drop within the reaction
438 zone. Making an comparison with the data reported by Ref.[9],
439 it can be observed that such critical temperature point depends
440 on fuel types. As shown by Fig. 2(c) in Ref.[9], while $T_{oxi} = 5.0$
441 there is still a slight temperature peak in hydrogen-air HDDI
442 combustion. The temperature rise of reactants $\Delta T = T_{max} - T_{oxi}$
443 is plotted by Fig. 4. Through this figure, it can be concluded
444 that ΔT is a monotonic decreasing function of T_{oxi} , except the
445 cases in which reaction can not be ignited (e.g. when $\varphi < 0.5$
446 and $T_{oxi}/T_0 < 2.0$). These features are similar with its hydro-
447 gen counterpart reported in Ref.[9] except two differences: (1) as
448 hydrogen is more active than methane, obvious temperature rise
449 can be observed even when $\varphi \leq 0.4$, but not for its methane
450 counterpart; (2) the decreasing rates of ΔT in methane-air HD-
451 DI combustion and its hydrogen counterpart are different. These
452 differences imply combustion regimes depending closely on fuel
453 types. In Ref.[7] Cavaliere et al. assumed that the classification of

454 various combustion regimes might rely on fuels used. The present
455 results can confirm their assumption.

456 According to Fig. 4, we can depict the map of different combus-
457 tion regimes in methane-air HDDI configuration, as illustrated by
458 Fig. 5. In Fig. 5, φ and T_{oxi} are chosen as the coordinates. The
459 benefits to adopt them to classify different combustion regimes
460 have been discussed in our previous work [9]. Similar with its hy-
461 drogen counterpart discussed in our previous study [9], there are
462 five combustion regimes in methane-air HDDI combustion con-
463 dition, as defined by Table 2. The detailed explanation on Table
464 2 is presented in Ref.[9]. Through a comparison between Fig. 5
465 in the present work and Fig.4 in Ref.[9], one can observe there
466 are four obvious differences between the combustion regimes of
467 methane-air HDDI configuration and those of its hydrogen coun-
468 terpart. Firstly, the transient regime, namely the "Flameless"
469 regime, is much narrower in methane-air HDDI combustion than
470 its hydrogen counterpart. Especially, without preheating there is
471 no "Flameless" regime in the former. Secondly, the zone of "No

Table 2

The classification of different combustion regimes for for methane-air HDDI combustion.

Combustion mode	Inlet conditions	Working conditions
Feedback combustion	$T_{oxi} < T_{si}$	$\Delta T > T_{si}$
HiTAC	$T_{oxi} > T_{si}$	$\Delta T > T_{si}$
Mild combustion	$T_{oxi} > T_{si}$	$\Delta T < T_{si}$
"Flameless"	$T_{oxi} < T_{si}$	$\Delta T \geq T_{si} - T_{oxi}$

472 Combustion" regime is larger in methane-air HDDI combustion,
 473 compared with its hydrogen counterpart. Thirdly, in methane-air
 474 HDDI combustion, the "MILD Combustion" regime exists nearly
 475 impossibly in the fuel-rich region but it is not true for its hydro-
 476 gen counterpart. Finally, in methane-air HDDI combustion, the
 477 "Feedback Combustion" regime can emerge in the fuel-lean re-
 478 gion while it is nearly impossible in its hydrogen counterpart.
 479 Consequently, in air-firing condition, compared with hydrogen, it
 480 is more complicated for methane to organize and sustain MILD
 481 combustion. More important, one should bear in mind that fu-
 482 el types will influence the pathway to MILD combustion regime
 483 critically. Especially for practical furnaces where a high preheat-
 484 ing temperature is restricted for safety reasons.

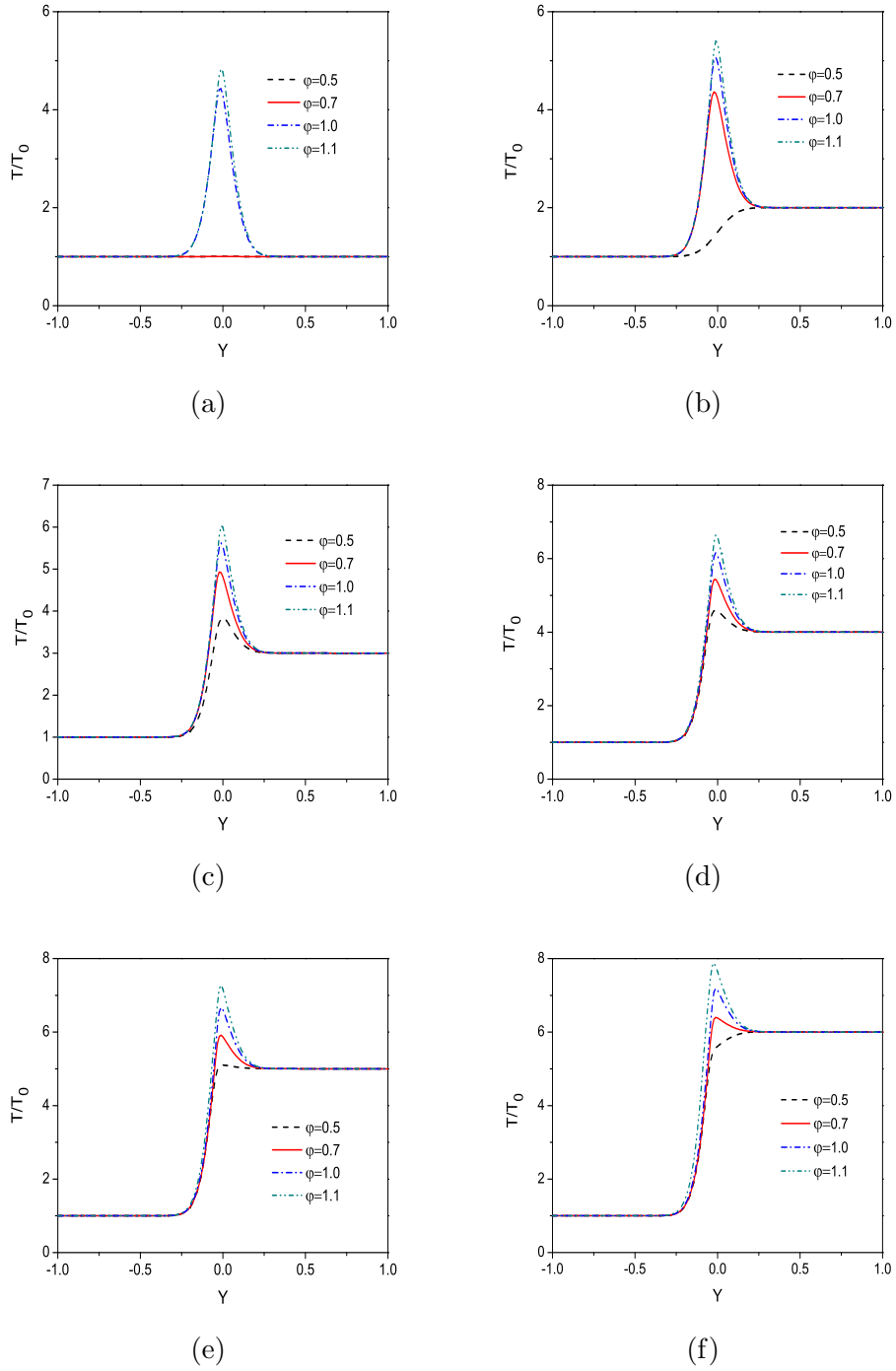


Fig. 2. Distributions of temperature with different φ along line $x = 0$ in air-firing condition: (a) $T_{oxi}/T_0 = 1$ (b) $T_{oxi}/T_0 = 2$ (c) $T_{oxi}/T_0 = 3$ (d) $T_{oxi}/T_0 = 4$ (e) $T_{oxi}/T_0 = 5$ (f) $T_{oxi}/T_0 = 6$.

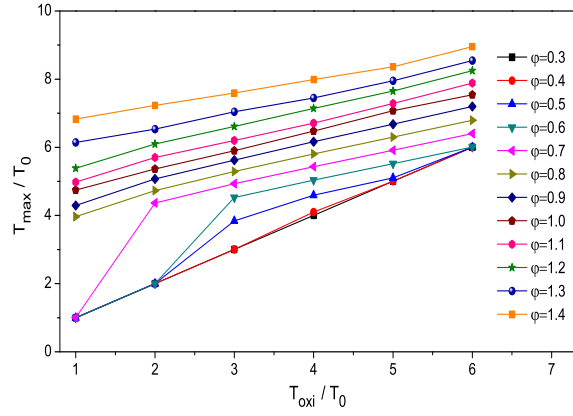


Fig. 3. Variations of maximum temperature of reactants, methane-air configuration.

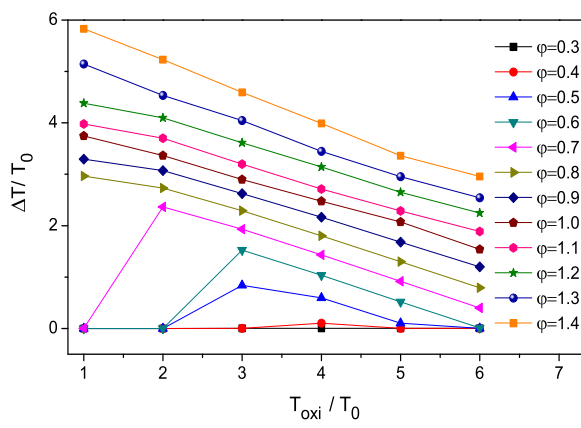


Fig. 4. Temperature rise of reactants, methane-air configuration.

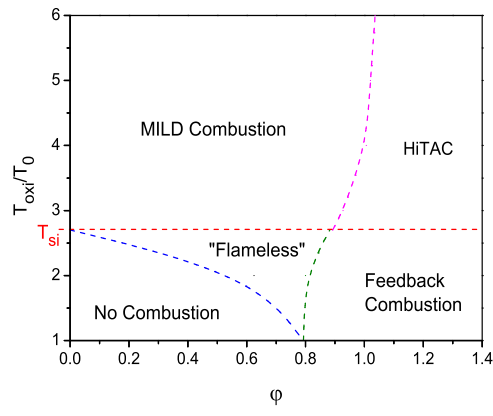


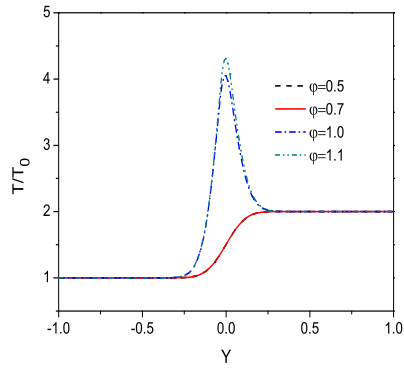
Fig. 5. Combustion regimes presented in $\phi - T_{oxi}$ map: air-firing condition.

485 4.1.2 *Temperature profiles in oxyfuel condition and comparison between dif-*
486 *ferent dilution atmosphere*

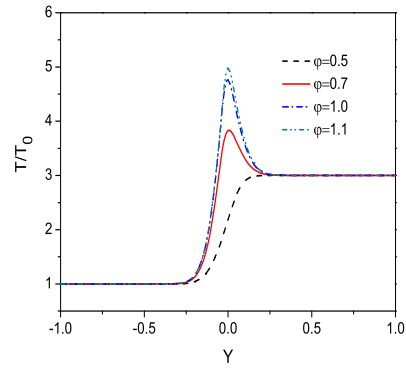
487 Figure 6 illustrates the temperature profiles at various equiva-
488 lence ratio and preheating temperature of oxidant flow in oxy-
489 fuel condition. Different from its air-firing counterpart discussed
490 above, in oxyfuel condition, oxygen in the oxidant flow is diluted
491 by CO₂ instead of nitrogen. As the specific heat capacity of CO₂
492 is bigger than air, the peak values of temperature of the reactants
493 are much lower than those in air-firing condition (c.f. Fig. 2). Es-
494 pecially, without preheating, combustion can not be sustained in
495 CO₂/O₂ atmosphere when $\varphi < 1.33$. More important, it can be
496 observed that the reaction zone in oxyfuel condition will hardly
497 expand with φ increasing, which results from the lower diffusive
498 coefficients of reactants in CO₂ atmosphere. In our previous study
499 [43], we analyzed the physical and chemical effects of CO₂ on re-
500 action characteristics and concluded the physical effect of CO₂
501 played a predominant role. The present observation agrees with
502 this conclusion. In addition, due to the large specific heat capac-

ity of CO_2 , there will not appear a local "hotspot" in the highly diluted fuel region (namely $\varphi < 0.5$), no matter whatever T_{oxi} is. With a high preheating temperature, if in fuel-lean condition, the heat released by the exothermic reactions may be much smaller than the energy borne by the preheated oxidant flow, which will cause a temperature drop within the reaction zone instead of a temperature jump, as shown by Fig. 6 (e). This phenomenon also exists in its air-firing counterpart.

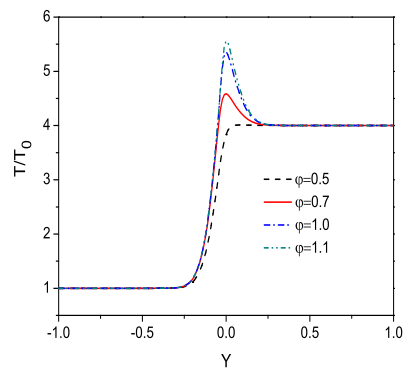
The maximum temperature of reactants T_{max} in oxyfuel condition is plotted in Fig. 7. According to this figure, one can observe that T_{max} is a monotonic increasing function of T_{oxi} and φ , similar with its air-firing counterpart. In addition, in the highly diluted fuel region, the lines of T_{max} with various φ almost overlap with each other as the heat released by exothermic reactions is too slight to induce temperature fluctuation, which also can be observed in its air-firing counterpart. However, their differences are obvious, too. Due to the high specific heat capacity of CO_2 , local "hotspots" can be suppressed in oxyfuel condition.



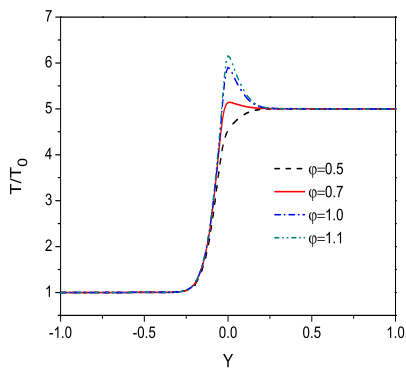
(a)



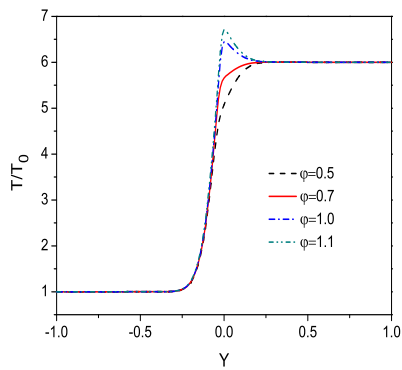
(b)



(c)



(d)



(e)

Fig. 6. Distributions of temperature with different φ along line $x = 0$ in oxyfuel condition: (a) $T_{oxi} = 2$ (b) $T_{oxi} = 3$ (c) $T_{oxi} = 4$ (d) $T_{oxi} = 5$ (e) $T_{oxi} = 6$.

521 For example, there is no obvious temperature jump for $\varphi = 0.6$

522 in oxyfuel condition but in its air-firing counterpart there will

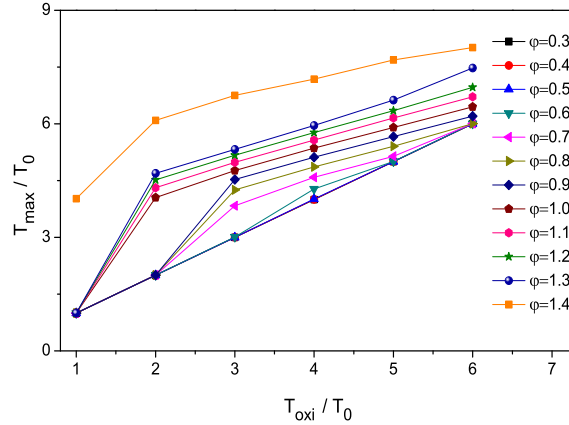


Fig. 7. Variations of maximum temperature of reactants, methane-oxyfuel configuration.

523 appear a significant temperature rise even when $\varphi = 0.5$. More-

524 over, in methane-oxyfuel HDDI combustion, T_{max} will experience

525 a "jump" when φ increases from 1.3 to 1.4 (as illustrated by Fig.

526 7, the gap between the contour $\varphi = 1.3$ and the contour $\varphi = 1.4$

527 is obviously larger than others). On the contrary, the variation

528 of T_{max} versus φ is "smooth" in its air-firing counterpart. Figure

529 8 shows the temperature rise of reactants. In oxyfuel condition,

530 ΔT will decrease linearly against T_{oxi} , similar with its air-firing

531 counterpart, although the decreasing speed in oxyfuel condition

532 is slower.

533 With Fig. 8, the map of different combustion regimes in oxy-

534 fuel condition can be plotted, as shown by Fig. 9. Through a

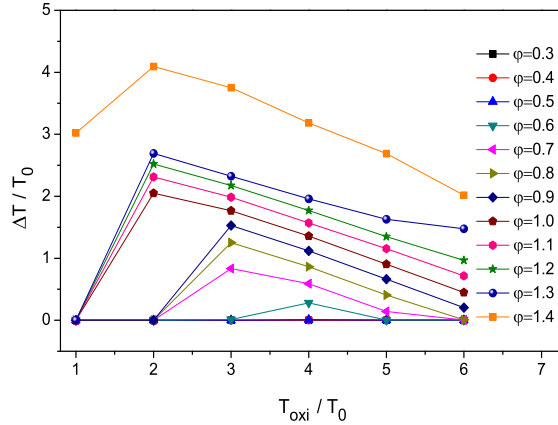


Fig. 8. Temperature rise of reactants, methane-oxyfuel configuration.

535 comparison between Fig. 5 and Fig. 9, some claims in previous
 536 publications can be explained straightforwardly. For instance, in
 537 Ref.[20] it was claimed that MILD combustion could be main-
 538 tained more easily in CO_2/O_2 atmosphere. As shown by Fig. 9,
 539 in oxyfuel condition, the "MILD Combustion" regime occupies
 540 a larger area than in air-firing condition, so MILD combustion
 541 can be sustained over a wider operational range accordingly. It
 542 is important for practical applications because in which obvious
 543 fluctuation of concentration of reactants is inevitable. Further-
 544 more, a theoretical explanation can be drawn to support why
 545 the best pathway to safely and effectively organize the "MILD
 546 Combustion" regime in oxyfuel condition (namely the so-called
 547 MILD oxyfuel combustion) is to start from air-firing condtion. In

548 our previous experimental efforts [54], we drew such conclusion
549 empirically without a clear theoretical support. As illustrated by
550 Fig. 9, compared with its air-firing counterpart (c.f. Fig. 5) the
551 "No Combustion" regime also occupies a larger area in oxyfuel
552 condition, which expands even to the fuel-rich region. It implies
553 that the possibility of extinction is very high if we run a cold fur-
554 nace in CO_2/O_2 atmosphere at the beginning. However, it is rela-
555 tively easy to guarantee stable combustion in air-firing condition,
556 even in the fuel-lean region. For practical applications, consider-
557 ing safety reasons, the preheating temperature is restricted not
558 too high. To meet this restriction, in the first stage we should
559 operate a furnace to reach the "Feedback Combustion" regime
560 in air-firing condition. Then we can shift to oxyfuel condition
561 through replacing air by CO_2/O_2 . The combustion will switch to
562 the "Flameless" regime automatically (please keep in mind that a
563 part of the "Feedback Combustion" regime in air-firing condition
564 overlaps with that of the "Flameless" regime in oxyfuel condi-
565 tion as the "Flameless" regime expands in oxyfuel condition).

566 Finally, we may approach to the "MILD Combustion" regime
567 through further preheating the oxidant flow by hot exhaust gas.
568 According to the maps depicted in Figs. 5 and 9, one also can
569 identify the crucial step in the above processes is the transition
570 from the "Feedback Combustion" regime in air-firing condition
571 to the "Flameless" regime in oxyfuel condition as this step may
572 meet the hazard of extinction in an industrial furnace. It is well-
573 known in a practical furnace heat loss is inevitable. As shown in
574 our previous work [9], the critical condition that the "Flameless"
575 regime can be sustained is that the heat released by exothermic
576 reactions could accumulate to ignite the fresh reactants as in the
577 "Flameless" regime the preheating temperature of the oxidan-
578 t flow is lower than the ignition temperature. If the heat loss
579 of a furnace overweighs the heat accumulation, the "Flameless"
580 regime will collapse and it is impossible to approach to the "MILD
581 combustion" regime. The furnace will fall into the "No Combus-
582 tion" regime and a safety accident has to be faced. With these
583 maps, one may design another pathway to reach MILD oxyfuel

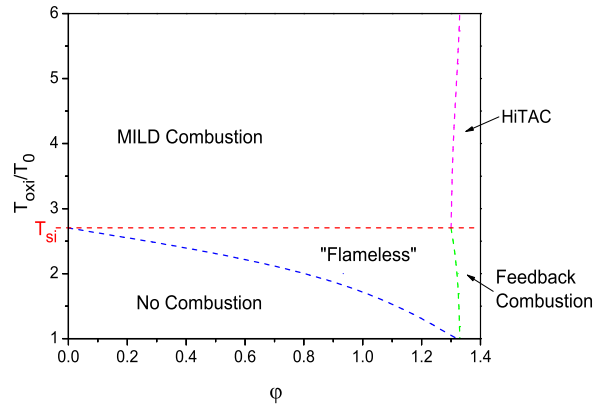


Fig. 9. Combustion regimes presented in $\varphi - T_{oxi}$ map: oxyfuel combustion condition.

584 combustion through crossing the "HiTAC" regime. Unfortunately,
 585 ly, such pathway is not cost-effective for practical applications
 586 as the requirements of material for furnace construction and the
 587 consumption of fuels for industrial operation are too high. More-
 588 over, as discussed below, along a transition pathway crossing the
 589 boundary between the "HiTAC" regime and the "MILD Com-
 590 bustion" regime, one has to pay great attention on the abrupt
 591 change of temperature distribution and its negative influence on
 592 combustion stability.

593 In addition, through the present work, it is found that, for methane
 594 oxyfuel HDDI combustion, there is a critical value of φ . As illus-
 595 trated by Fig. 7, the critical value is $\varphi \approx 1.3$. A small fluctuation

596 around the critical value will cause abrupt changes of tempera-
597 ture profiles and reaction structures, as shown by Fig. 7. Being
598 reflected on the map of combustion regimes, it corresponds with
599 a sharp-cliff-like boundary between combustion regimes (e.g. the
600 boundary between the "MILD Combustion" regime and the "Hi-
601 TAC" regime in Fig. 9). In hydrogen HDDI combustion, there
602 is not a critical value of φ (i.e. any small fluctuation of hydrogen
603 concentration will not cause an abrupt change of temperature
604 profiles and reaction structures, as shown by Fig.3 in Ref.[9]),
605 so the boundary between the "MILD Combustion" regime and
606 the "HiTAC" regime looks like a gentle slope, as illustrated by
607 Fig.4 in Ref.[9]. It is a new interesting finding that there is a re-
608 lationship between a sharp-cliff-like boundary in the map and a
609 critical value of φ in combustion. This finding may be very useful
610 for practical operation. For example, with the maps shown by
611 Fig.9 at hand, if one observe a methane-fed combustion system
612 is run at a state near the sharp-cliff-like boundary between com-
613 bustion regimes, for safety it is reasonable to act immediately to

614 escape the state, avoiding potentially abrupt changes due to a
615 small fluctuation. An open question emerges: whether this con-
616 clusion can be extended to other fuels? Further investigation is
617 desired to answer it. If so, the purposes of a combustion regime
618 classification map can be extensively expanded, not only to be
619 used to design a feasible pathway to reach a destination com-
620 bustion regime, but also to be adopted as an safety indicator for
621 practical operation.

622 *4.2 Influences of fuel type and dilution atmosphere on entropy generation in*
623 *various combustion regimes*

624 The above-mentioned discussions all are based on the first law
625 of thermodynamics. During the past decades, entropy generation
626 analysis stemmed from the second law of thermodynamics has be-
627 come a powerful tool for combustion optimization [57,58]. How-
628 ever, a comprehensive analysis on the effects of fuel types and
629 dilution atmosphere on entropy generation in various combus-
630 tion regimes is absent yet. In this subsection entropy generation

631 analysis is firstly carried out for methane-air HDDI combustion.
632 Then a comparison is made with the results presented in our
633 previous publication [9] to reveal the influences of different fuels
634 on entropy generation in various combustion regimes. In succes-
635 sion, a comparison between methane-air HDDI combustion and
636 methane-oxyfuel HDDI combustion is conducted to show the ef-
637 fects of different dilution atmosphere.

638 4.2.1 Entropy generation in air-firing condition

639 Figure 10 illustrates the variation of S_{total} with different φ in
640 air-firing condition, where the cases with $T_{oxi} = 1, 2, 6$ are cho-
641 sen as the representatives. Although S_{total} is always a monotonic
642 increasing function of φ , the increasing rates in various combus-
643 tion regimes are quite different. In the "No Combustion" regime,
644 S_{total} is slight as where the only contributors to exergy loss are
645 the irreversibility due to fluid friction and due to mass transfer.
646 In both the "Flameless" regime and the "MILD Combustion"
647 regime, S_{total} grows relatively slowly with φ . While in the "Hi-

648 TAC” regime or the ”Feedback Combustion” regime, S_{total} ris-
649 es sharply. What should be mentioned is the increasing rate of
650 S_{total} in the ”Feedback Combustion” regime is faster than that
651 in the ”HiTAC” regime. In the fuel-lean region, no matter in
652 which combustion regime, a higher preheating temperature will
653 cause more irreversibility because when fuel is insufficient a high-
654 er preheating temperature can enhance chemical reaction as well
655 as temperature difference. Accordingly, the irreversibility due to
656 chemical reaction and heat transfer will be intensified. However,
657 in the ”HiTAC” regime, a higher T_{oxi} can suppress irreversibility
658 generation, as shown in Fig.11. This observation indicates that
659 in the ”HiTAC” regime the irreversibility due to heat transfer
660 becomes the predominant contributor to exergy loss, as a high-
661 er T_{oxi} can reduce the temperature difference near the reaction
662 zone, which can decrease the irreversibility due to heat transfer
663 accordingly. Furthermore, one can conclude that in the fuel-lean
664 region, no matter in which combustion regime, the irreversibility
665 due to chemical reaction is the predominant contributor to exergy

666 loss. These findings are helpful to optimize a combustion system
667 as the first and crucial step for combustion system optimization
668 is to identify the dominant contributors to entropy generation
669 [58,59].

670 Compared with the results presented in Ref.[9] where hydrogen-
671 air HDDI combustion was investigated, it can be observed that
672 there are some common features of entropy generation between
673 hydrogen and methane in air-firing condition: (1) S_{total} is always
674 a monotonic increasing function of φ (Fig.10 in Ref. [9]); (2) in
675 the "HiTAC" regime the irreversibility due to heat transfer is
676 the major contributor to exergy loss (Fig.12 in Ref. [9]). Howev-
677 er, from the viewpoint of entropy production analysis, the differ-
678 ences between them are also obvious. Firstly, as shown by Fig.10
679 in Ref. [9], S_{total} grows almost linearly with φ in hydrogen-air
680 HDDI combustion. Moreover, the lines in that figure are nearly
681 parallel with each other. It implies that for hydrogen-air HD-
682 DI combustion the increasing rates of S_{total} in all combustion
683 regimes are nearly the same and insensitive to T_{oxi} . However, as

684 shown by Fig.10 in the present work, it can be observed that
685 for its methane counterpart the influence of combustion regimes
686 on variation of S_{total} is complicated and the variation speed of
687 S_{total} depends closely on T_{oxi} . Secondly, as illustrated by Fig.12
688 in Ref. [9], for hydrogen-air HDDI combustion in the fuel-lean
689 region, the major contributor to entropy generation is not always
690 the irreversibility due to chemical reaction. In the "Flameless"
691 regime, the irreversibility due to chemical reaction occupies a
692 great share, similar with its methane counterpart. However, in
693 the "MILD Combustion" regime, the irreversibility due to chem-
694 ical reaction and that due to heat transfer compete with each
695 other. The major contributor to exergy destroy depends closely
696 on T_{oxi} . It is quite different form its methane counterpart. Thirdly,
697 recently Soroudi and Ghafourian [60] investigated entropy gener-
698 ation in the "HiTAC" regime and "MILD Combustion" regime
699 of methane-air HDDI combustion and they concluded that the
700 intensity of irreversibility generation, namely the maximum val-
701 ue of local entropy generation number S_{max} , would decrease as

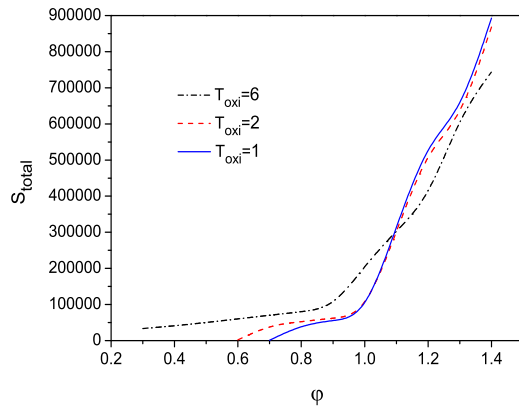


Fig. 10. Variation of S_{total} with different ϕ and T_{oxi} in air-firing condition.

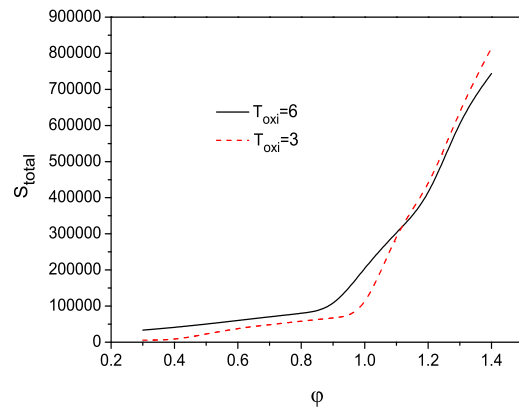


Fig. 11. Variation of S_{total} with different ϕ and T_{oxi} in "MILD Combustion" and "HiTAC" regimes.

702 the dilution becomes more intense. Fig.12 in the present work a-
 703 grees well with their conclusion. In addition, The present results
 704 can demonstrate this conclusion can hold water for all combus-
 705 tion regimes in methane-air HDDI condition. However, as shown
 706 by Fig.10 in Ref. [9], this conclusion is not always true for its
 707 hydrogen counterpart.

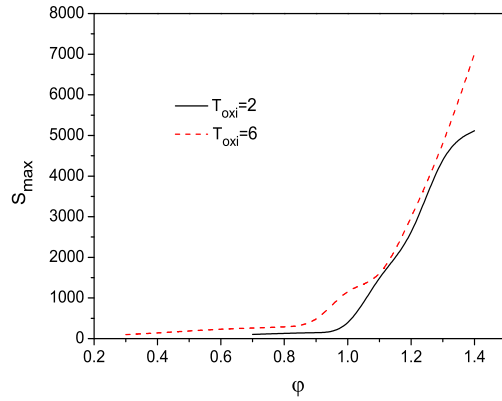


Fig. 12. Variation of S_{max} with different φ and T_{oxi} .

708 *4.2.2 Entropy generation in oxyfuel condition*

709 The variation of S_{total} in oxyfuel condition is depicted by Fig.13.

710 It can be observed that S_{total} is always a monotonic increasing

711 function of φ in all combustion regimes although the increasing

712 rates in various regimes are different. In the "No Combustion"

713 regime, S_{total} is slight as where the only contributors to exer-

714 gy loss are the irreversibility due to fluid friction and due to

715 mass transfer. In both the "Flameless" regime and the "MILD

716 Combustion" regime, S_{total} grows relatively slowly with φ . While

717 in the "HiTAC" regime or the "Feedback Combustion" regime,

718 S_{total} climbs up sharply. These features in oxyfuel condition are

719 the same as its air-firing counterpart. However, the differences

720 between them are also obvious. Firstly, in air-firing condition,
721 S_{total} in the "Feedback Combustion" regime will exceed that in
722 the "HiTAC" regime while in oxyfuel condition it is not the truth.
723 Secondly, as shown by Fig.14, in the "HiTAC" regime, S_{total} with
724 a higher T_{oxi} is always larger than that with a lower T_{oxi} . It is
725 completely contrary to its air-firing counterpart. According to
726 Figs.13-14, it can be concluded that in oxyfuel condition, in al-
727 l combustion regimes, a higher T_{oxi} corresponds a bigger S_{total} .
728 This conclusion implies that in oxyfuel condition the irreversibili-
729 ty due to chemical reaction is always the major contributor to ex-
730 ergy destroy, no matter in which combustion regime. This feature
731 is different from its air-firing counterpart where the irreversibility
732 due to chemical reaction and that due to heat transfer are com-
733 petitive. Finally, S_{total} in oxyfuel condition is much lower than
734 its air-firing counterpart because temperature jump near the re-
735 action zones (c.f. Figs. 2 and 6), as well as reaction rates (the
736 details please refer to our previous publications [43,51]), is small-
737 er in CO₂/O₂ atmosphere. Consequently, the irreversibility due

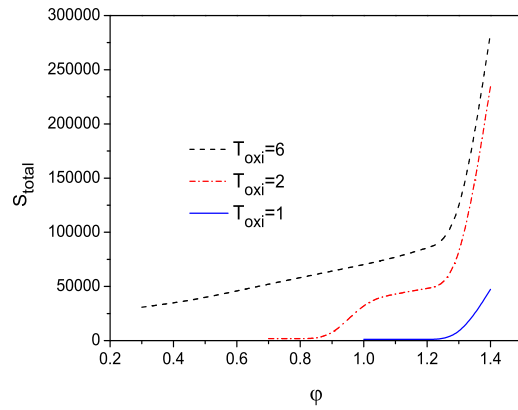


Fig. 13. Variation of S_{total} with different φ and T_{oxi} in oxyfuel condition.

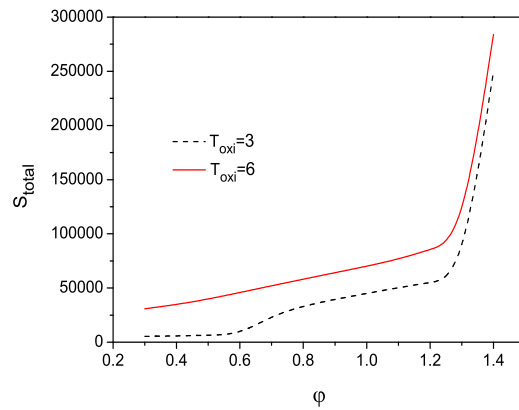


Fig. 14. Variation of S_{total} with different φ and T_{oxi} in "MILD Combustion" and "HiTAC" regimes.

738 to chemical reaction and that due to heat transfer both descend.

739 Figure 15 illustrates the variation of S_{max} with different φ and

740 T_{oxi} . Through this figure, one can observe that the intensity of

741 irreversibility generation descends as the dilution become more

742 intense. Namely, the conclusion drawn in air-firing condition[60]

743 can be extended to its oxyfuel counterpart. It also can be ob-

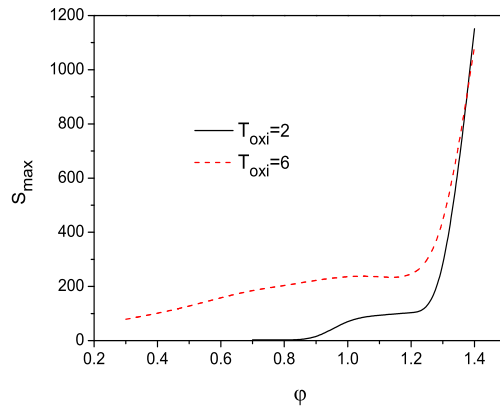


Fig. 15. Variation of S_{max} with different φ and T_{oxi} .

744 served that S_{max} in oxyfuel condition is much smaller than its
 745 air-firing counterpart and the reason has been given above. A d-
 746 ifference between them is illustrated by Fig.15. In the figure, one
 747 can observe that the gap between the lines becomes to dimin-
 748 ish in the "HiTAC" regime. It implies in the "HiTAC" regime of
 749 oxyfuel condition the irreversibility due to heat transfer becomes
 750 as important as that due to chemical reaction.

751 Finally, according to Figs.10, 12, 13 and 15, one also can con-
 752 clude that a transition pathway from the "HiTAC" regime to
 753 the "MILD Combustion" (or MILD oxyfuel) regime is not eco-
 754 nomical, from the viewpoint of the second thermodynamic-law,
 755 as more entropy (namely exergy destroy) will be generated a-

756 long such pathway. The most economical pathway is crossing the
757 "Flameless" regime, which agrees with the above result obtained
758 from the viewpoint of the first thermodynamic-law. Consequent-
759 ly, the first and second thermodynamic-law analyses on the maps
760 of combustion regimes both can provide a consistent theoretical
761 guide on how to design an efficient way to establish and to sus-
762 tain "MILD Combustion" (or MILD oxyfuel) regime, from the
763 standpoint of safety and of cost, respectively.

764 **5 Conclusion**

765 The idea of MILD oxyfuel combustion has attracted increasing
766 attention as a clean approach to utilize fossil fuels. However, it
767 is impossible to establish MILD oxyfuel combustion directly. In
768 the present study, we try to address this challenge with the aid
769 of combustion regime maps. The major findings of the present
770 investigation can be summarized as:

771 (1) Through a comparison between the combustion regime map-

772 s, an efficient pathway to establish and sustain MILD oxyfuel
773 combustion can be determined, which agrees with our empirical
774 experiences.

775 (2) Through the present work, it can be observed that the ef-
776 fects of fuel type and dilution atmosphere on combustion regime
777 classification are significant.

778 (3) With the aid of the second thermodynamic-law analysis, the
779 major contributors to exergy loss can be identified clearly.

780 (4) The purposes of a map of combustion regime classification are
781 extensively expanded by this work. Besides being used to design
782 a pathway to establish MILD combustion, the map also can be
783 adopted as a safety indicator for combustion operation.

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794 **References**

- 795 [1] IEA (2015), World Energy Outlook Special Report: Energy and Climate
796 Change, OECD/IEA, Paris.
- 797 [2] Cavaliere A, de Joannon M. Mild Combustion. Progress in Energy and
798 Combustion Science 2004; 30: 329-366.
- 799 [3] Buhre BJP, Elliott LK, Sheng CD, Gupta RP, Wall TF. Oxy-fuel combustion
800 technology for coal-fired power generation. Progress in Energy Combust Science
801 2005;31:283-307.
- 802 [4] Cavigiolo A, Galbiati M A, Effuggi A, Gelosa D, Rota R. Mild combustion in a
803 laboratory-scale apparatus. Combustion Science and Technology 2003;175:1347-
804 1367
- 805 [5] Galbiati MA, Cavigiolo A, Effuggi A, Gelosa D, Rota R. Mild combustion for
806 fuel-NOx reduction. Combustion Science and Technology 2004;176:1035-1054

- 807 [6] De Joannon M, Matarazzo A, Sabia P, Cavaliere A. MILD combustion in
808 homogeneous charge diffusion ignition (HC DI) regime. Proceedings of the
809 Combustion Institute. 2007;:3409-3416.
- 810 [7] De Joannon M, Sabia P, Sorrentino G, Cavaliere A. Numerical study of mild
811 combustion in hot diluted diffusion ignition (HDDI) regime. Proceedings of the
812 Combustion Institute. 2009;32:3147-3154.
- 813 [8] de Joannon M, Sorrentino G, Cavaliere A. MILD combustion in diffusion-
814 controlled regimes of Hot Diluted Fuel. Combustion and Flame 2012;159:1832-
815 1839
- 816 [9] Chen S, Mi J, Liu H, Zheng C. First and second thermodynamic-law analyses of
817 hydrogen-air counter-flow diffusion combustion in various combustion modes.
818 International Journal of Hydrogen Energy 2012;37:5234-5245
- 819 [10] Wang F, Mi J, Li P. Combustion Regimes of a Jet Diffusion Flame in Hot
820 Co-flow. Energy Fuels 2013;27:3488-3498
- 821 [11] Evans MJ, Medwell PR, Wu H, Stagni A, Ihme M. Classification and lift-off
822 height prediction of non-premixed MILD and autoignitive flames. Proceedings
823 of the Combustion Institute (in press) doi:10.1016/j.proci.2016.06.013
- 824 [12] Szego GG, Dally BB, Nathan GJ. Operational characteristics of a parallel jet
825 MILD combustion burner system. Combustion and Flame 2009;156: 429-438
- 826 [13] Dally BB, Karpetis AN, Barlow RS. Structure of turbulent non-premixed jet
827 flames in a diluted hot coflow. Proceedings of the Combustion Institute 2002;29:
828 1147-1154

- 829 [14] Weber R, Smart JP, Kamp W. On the (MILD) combustion of gaseous,
830 liquid, and solid fuels in high temperature preheated air. Proceedings of the
831 Combustion Institute 2005;30:2623-2629.
- 832 [15] Effuggi A, Gelosa D, Derudi M, Rota R. Mild combustion of methane derived
833 fuel mixtures: natural gas and biogas. Combustion Science and Technology
834 2008;180: 481-493.
- 835 [16] Tu Y, Liu H, Chen S, Liu Z, Zhao H, Zheng C. Effects of furnace chamber
836 shape on the MILD combustion of natural gas. Applied Thermal Engineering
837 2015;76:64-75
- 838 [17] Noor MM, Wandel AP, Yusaf T. MILD Combustion: The Future for Lean and
839 Clean Combustion Technology. International Review of Mechanical Engineering
840 2014;8:251-257
- 841 [18] Kim JP, Schnell U, Scheffknecht G. Comparison of Different Global Reaction
842 Mechanisms for MILD Combustion of Natural Gas. Combustion Science and
843 Technology 2008;180:565-592
- 844 [19] Wang L, Chen S, Liu Z, Zheng CG. Comparison of Different Global Combustion
845 Mechanisms for Use in CFD Modeling under Hot and Diluted Oxidation
846 Condition. Combustion Science and Technology 2012;184:259-276
- 847 [20] Chen S, Zheng CG. Counterflow diffusion flame of hydrogen-enriched biogas
848 under MILD oxy-fuel condition. International Journal of Hydrogen Energy
849 2011;36:15403-15413.
- 850 [21] Hamdi M, Benticha H, Sassi M. Evaluation of reduced chemical kinetic

- 851 mechanisms used for modeling mild combustion for natural gas. *Thermal*
852 *Science* 2009;13: 131-137
- 853 [22] Galletti C, Parente A, Derudi M, Rota R, Tognotti L. Numerical and
854 experimental analysis of NO emissions from a lab-scale burner fed with
855 hydrogen-enriched fuels and operating in MILD combustion. *International*
856 *Journal of Hydrogen Energy* 2009;34: 8339-8351
- 857 [23] Mardani A, Tabejamaat S. NO_x Formation in H₂-CH₄ Blended Flame Under
858 MILD Conditions. *Combustion Science and Technology* 2012;184:995-1010
- 859 [24] Li P, Wang F, Mi J, Dally BB, Mei Z, Zhang J, Parente A. Mechanisms of NO
860 formation in MILD combustion of CH₄/H₂ fuel blends. *International Journal*
861 *of Hydrogen Energy* 2014;39:19187-19203
- 862 [25] Loffler G, Sieber R, Harasek M, Hofbauer H, Hauss R, Landauf J. NO_x
863 formation in natural gas combustion-a new simplified reaction scheme for CFD
864 calculations. *Fuel* 2006;85: 513-523
- 865 [26] Galletti C, Ferrarotti M, Parente A, Tognotti L. Reduced NO formation models
866 for CFD simulations of MILD combustion. *International Journal of Hydrogen*
867 *Energy* 2015;40: 4884-4897
- 868 [27] Bozzelli JW, Dean AM. O+NNH: A possible new route for NO_x formation in
869 flames. *International Journal of Chemical Kinetics* 1995;27:1097-1109
- 870 [28] Konnov A, Colson G, Ruyck JD. The new route forming NO via NNH.
871 *Combustion and Flame* 2000;121(3):548-550

- 872 [29] Nicolle A, Dagaut P. Occurrence of NO-reburning in MILD combustion
873 evidenced via chemical kinetic modeling. *Fuel* 2006;85:2469-2478
- 874 [30] Parente A, Galletti C, Tognotti L. A simplified approach for predicting NO
875 formation in MILD combustion of CH₄-H₂ mixtures. *Proceedings of the*
876 *Combustion Institute* 2011;33: 3343-3350
- 877 [31] Fortunato V, Galletti C, Tognotti L, Parente A. Influence of modelling and
878 scenario uncertainties on the numerical simulation of a semi-industrial flameless
879 furnace. *Applied Thermal Engineering* 76 (2015), 324- 334.
- 880 [32] Mi J, Li P, Dally BB, Craig RA. Importance of initial momentum rate and air-
881 fuel premixing on moderate or intense low oxygen dilution (MILD) combustion
882 in a recuperative furnace. *Energy and Fuel*. 2009;23:5349-5356.
- 883 [33] Mardani A, Tabejamaat S, Ghamari M. Numerical study of molecular diffusion
884 in the MILD combustion regime. *Combustion Theory and Modelling*. 2010;
885 14:747-774
- 886 [34] Aminian J, Galletti C, Tognotti L. Extended EDC local extinction model
887 accounting finite-rate chemistry for MILD combustion. *Fuel* 2016;165:123-133
- 888 [35] Parente A, Malik MR, Contino F, Cuoci A, Dally BB. Extension of the
889 Eddy Dissipation Concept for turbulence/chemistry interactions to MILD
890 combustion. *Fuel* 2016;163:98-111
- 891 [36] Hosseini SE, Wahid MA. Enhancement of exergy efficiency in combustion
892 systems using flameless mode. *Energy Conversion and Management* 2014; 86:
893 1154-1163

- 894 [37] Hosseini SE, Bagheri G, Wahid MA. Numerical investigation of biogas flameless
895 combustion. *Energy Conversion and Management* 2014;81:41-50
- 896 [38] Budzianowski WM. An oxy-fuel mass-recirculating process for H₂ production
897 with CO₂ capture by autothermal catalytic oxyforming of methane.
898 *International Journal of Hydrogen Energy* 2010;35:7454-7469
- 899 [39] Toftegaard MB, Brix J, Jensen PA, Glarborg P, Jensen AD. Oxy-fuel
900 combustion of solid fuels. *Progress in Energy and Combustion Science*
901 2010;36:581-625
- 902 [40] Krishnamurthy N, Paul PJ, Blasiak W. Studies on low-intensity oxy-fuel burner.
903 *Proceedings of the Combustion Institute* 2009;32:3139-3146
- 904 [41] Khare SP, Wall TF, Farida AZ, Liu Y, Moghtaderi B, Gupta RP. Factors
905 influencing the ignition of flames from air-fired swirl pf burners retrofitted to
906 oxy-fuel. *Fuel* 2008;87:1042-1049
- 907 [42] Andersen J, Rasmussen CL, Giselsson T, Glarborg P. Global Combustion
908 Mechanisms for Use in CFD Modeling under Oxy-Fuel Conditions. *Energy*
909 *Fuels*, 2009;23:1379-1389
- 910 [43] Wang L, Liu Z, Chen S, Zheng C, Li J. Physical and Chemical Effects of CO₂
911 and H₂O Additives on Counterflow Diffusion Flame Burning Methane. *Energy*
912 *Fuels* 2013;27:7602-7611
- 913 [44] Pak PS, Lee YD, Ahn KY. Characteristics and economic evaluation of a power
914 plant applying oxy-fuel combustion to increase power output and decrease CO₂
915 emission. *Energy* 2010;35:3230-3238.

- 916 [45] Borgert KJ, Rubin ES. Oxyfuel Combustion: Technical and Economic
917 Considerations for the Development of Carbon Capture from Pulverized Coal
918 Power Plants. *Energy Procedia* 2013;37:1291-1300
- 919 [46] Normann F., K Andersson, B Leckner, Johnsson F. Emission control of nitrogen
920 oxides in the oxy-fuel process. *Progress in Energy and Combustion Science*
921 2009;35:385-397
- 922 [47] Chen L, Yong SZ, Ghoniem AF. Oxy-fuel combustion of pulverized coal:
923 Characterization, fundamentals, stabilization and CFD modeling. *Progress in*
924 *Energy and Combustion Science* 2012;38:156-214
- 925 [48] Yin C, Yan J. Oxy-fuel combustion of pulverized fuels: Combustion
926 fundamentals and modeling. *Applied Energy* 2016;162:742-762
- 927 [49] Lockwood T. Developments in oxyfuel combustion of coal, CCC/240 2014
- 928 [50] Li P, Dally BB, Mi J, Wang F. MILD oxy-combustion of gaseous fuels in a
929 laboratory-scale furnace. *Combust Flame* 2013;160:933-946.
- 930 [51] Liu Y, Chen S, Yang B, Liu K, Zheng C. First and second thermodynamic-law
931 comparison of biogas MILD oxy-fuel combustion moderated by CO₂ or H₂O.
932 *Energy Conversion and Management* 2015;106:625-634.
- 933 [52] Tu Y, Liu H., Chen S, Liu Z, Zhao H, Zheng C. Numerical study of combustion
934 characteristics for pulverized coal under oxy-MILD operation. *Fuel Processing*
935 *Technology* 2015;135: 80-90
- 936 [53] Mardani A, Ghomshi AF. Numerical study of oxy-fuel MILD (moderate or
937 intense low-oxygen dilution combustion) combustion for CH₄-H₂ fuel. *Energy*

938 2016;99:136-151

939 [54] Li P, Mi J, Dally BB, Wang F, Wang L, Liu Z, Chen S, Zheng C. Progress and
940 recent trend in MILD combustion. *Sci China Technol Sci* 2011;54:255-269.

941 [55] Chen S, Liu Z, Zhang C, He Z, Tian Z, Shi B. and Zheng C.G. A novel coupled
942 lattice Boltzmann model for low Mach number combustion simulation. *Applied*
943 *Mathematics and Computation* 2007;193: 266-284.

944 [56] Chen S, Li J, Han HF, Liu ZH, Zheng CG. Effects of hydrogen addition on
945 entropy generation in ultra-lean counter-flow methane-air premixed combustion.
946 *Int J Hydrogen Energy* 2010;35:3891-3902.

947 [57] A. Sciacovelli, V. Verda, E. Sciubba. Entropy generation analysis as a design
948 tool-A review. *Renewable and Sustainable Energy Reviews* 2015;43: 1167-1181

949 [58] H.R. Arjmandi, E. Amani. A numerical investigation of the entropy generation
950 in and thermodynamic optimization of a combustion chamber. *Energy* 2015;81:
951 706-718

952 [59] Jiang D, Yang W, Teng J. Entropy generation analysis of fuel lean premixed
953 CO/H₂/air flames. *International Journal of Hydrogen Energy*, 2015; 40:5210-
954 5220

955 [60] Soroudi MA, Ghafourian A. Entropy Generation and Exergy Loss in Natural
956 Gas Mild Combustion Process. *Processes and Technologies for a Sustainable*
957 *Energy* 2010; doi : 10.4405/ptse2010.P1.1.