Effects of H₂ and CO enrichment on the combustion, emission and performance characteristics of spark ignition natural gas engine

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Nomenclature:

ABDC:	after bottom dead center
ATDC:	after top dead center
BBDC:	before bottom dead center
BMEP:	brake mean effective pressure
BTDC:	before top dead center
CAD:	crank angle degree
CNG:	compressed natural gas
CFR:	catalytic fuel reforming
CovIMEP:	coefficient of variation of IMEP
ECU:	electronic control unit
EVC:	exhaust valve close
EVO:	exhaust valve open
IMEP:	indicated mean effective pressure
IVC:	intake valve close
IVO:	intake valve open
n:	engine speed
NHPR:	net heat production rate
NG:	natural gas
NVO:	negative valve open
p:	cylinder pressure
ST:	spark timing
Φ :	equivalence ratio
θ :	crank angle
θ_{ST} :	crank angle for spark timing
θ_{10} :	crank angle for 10 percent mass fraction burnt
θ_{90} :	crank angle for 90 percent mass fraction burnt
$\Delta\theta_{fd}$:	flame development duration
$\Delta\theta_{rd}$:	rapid combustion duration
η_e :	effective thermal efficiency
$dQ_{net}/d\theta$:	net heat release rate
[CO]:	CO emission concentration
[NO _x]:	NO _x emission concentration
[THC]:	total hydrocarbon emission concentration

Abstract

Fuel reforming is an attractive way for improving the performances of internal combustion engine. The primary components of the reformed gases are H_2 , CO, CO_2 and N_2 . A detailed knowledge of each component in reformed gas is essential for judging or making better use of the reformed gas as well as reforming technologies. In this paper, the influences of the major combustibles of the reformed gas, H_2 and CO, on the performance of a lean burn spark ignition natural gas engine are investigated. Results indicate that addition of H_2 and CO could improve in-cylinder combustion, smooth engine operation and increase engine thermal efficiency. With the addition of H_2 and CO, both the peaks of in-cylinder pressure and heat release rate increases, flame development duration and rapid combustion duration as well as CovIMEP decreases. However, CO is less effective compared with H_2 . The influence of H_2 on engine THC emission is insignificant while addition of CO tends to increase engine CO emission remarkably owing to the quenching and crevice effect. Both H_2 and CO tend to worsen engine NO_x emission due to the increased in-cylinder temperature while the effect of H_2 is more distinct. The simulation of laminar flame speed manifests that addition of H_2 and CO increase O, H and OH radical concentration and hence improve the flame propagation and the combustion process, resulting in improved laminar flame speed of the fuel-air mixtures. In compare, H_2 addition leads to higher laminar flame speed than CO addition does. The whole investigation of this paper implies that both H_2 and CO in the reformed gas are effective in improving engine combustion and effective thermal efficiency while H_2 is more effective.

Key words: Natural gas; H_2 ; CO; Combustion; Emission

1, Introduction

With the increasing concern about environmental pollution and growing demand for energy provision, natural gas is considered as an alternative fuel for petroleum based vehicle energy resources (diesel and gasoline) recently. Hence it has been widely investigated in engines [1-4] and even its main components (methane) was involved in some fundamental studies [5, 6]. Compared with diesel and gasoline, natural gas exhibits lower carbon emission for its high hydrogen carbon ratio [7], besides, it is free from aromatic compounds thus results in low PM emission [4]. In addition, natural gas is rich in reserves hence would lead to a stable market price. Therefore, nowadays, natural gas engine has been widely used in many fields like stationary power generation and transportation.

However, due to comparatively lower laminar flame speed [8], natural gas demonstrates a longer rapid combustion duration and poorer thermal efficiency than gasoline does. To enhance the combustion property and improve thermal efficiency of natural gas engine, many researchers have devoted to hydrogen-NG investigation over the past years [9-11]. Results showed that hydrogen addition into natural gas evidently improved engine combustion performance, enhanced thermal efficiency and lowered HC and CO emission while increased NO_x emission. Nevertheless, the latest investigation demonstrated that NO_x emission could be controlled through excess air ratio and spark timing collaborative optimization [12].

Actually, the fact that hydrogen addition improves engine efficiency and in-cylinder combustion property was also confirmed on other types of engines [13-15]. While, industrial hydrogen production is mainly through steam reforming using hydrocarbon fuel, which involves complex facilities, noble metal catalyst and purification process [16]. Consequently, pure

hydrogen could hardly be commercially used as vehicle fuel additive as it is not economic. Therefore, researchers gradually diverted to some more economically viable ways. As an alternative, onboard catalytic fuel reforming (CFR) was found to be effective for hydrogen production.

With proper catalysis and suitable temperature condition, hydrocarbon fuels could be reformed to combustible gas rich in H_2 through steam reforming, auto-thermal reforming or partial oxidation[17]. Steam reforming is more advantageous for improving engine performances not only due to its higher H_2 production, but also owing to its endothermic reaction which helps to energy recovery from engine exhaust. Ethanol and methanol were generally preferred as the reforming feedstock favored by their comparatively lower temperature requirement and thus were investigated by a number of researchers. Erik D. Sall et al. [18] demonstrated the feasibility of ethanol and methanol fuel reforming on automotive engine. Ji et al. [19, 20] used onboard steam reformed ethanol gas as a fuel additive on a gasoline engine. Results disclosed that engine thermal efficiency was improved and flame development and propagation duration were shortened. Moreover, HC and NO_x emissions were reduced while CO emission was increased under stoichiometric condition. L. Tartakovsky et al. [21, 22] investigated engine performances when running on ethanol and methanol steam reforming products and resulted in an increased engine thermal efficiency and decreased NO_x , THC and CO emission when compared with original gasoline engine.

Nevertheless, onboard fuel reforming technique could hardly be performed with some of the hydrocarbon fuels such as gasoline owing to high reforming temperature requirement[23]. Besides, catalyst deactivation caused by sulphur content in natural gas would also be a challenge for

onboard fuel reforming [24, 25]. To avoid these disadvantages, in-cylinder fuel reforming which involves reforming fuel using fuel rich combustion was proposed and conducted by a series of researchers. Terry Alger and Barrett Mangold [26, 27] proposed an in-cylinder reforming method on a gasoline engine which involves running one cylinder (or more cylinders) rich of stoichiometric and routing the all the exhaust (reformed product) of that cylinder back into the intake pipe. A portion of H_2 was found in the exhaust of the rich combustion cylinder and improved engine efficiency was resulted combined with decreased engine emission. Willand et al. [28] suggested a method which involves reforming fuel within high temperature residual retained in engine cylinder during negative valve overlap (NVO) duration and has been extensively used by numerous researchers in HCCI combustion [29-34]. And it was found that the reformed gas contained significant amount of H_2 [33, 34] and tended to expand HCCI operating range and stabilize engine running. Results from some other researchers again confirmed that the reformed gas during NVO was rich in H_2 [33, 35].

In the aforementioned reforming methods (onboard or in-cylinder reforming), H_2 is not the only the major component in the reformed gases, accompanied by significant amount of CO. Experiments conducted by Toshio Shudo et al. [36] showed that the production of CO was nearly half of H_2 in the methanol catalytic reformed gas (with CO_2 , CH_4 and CH_3OCH_3 being the minority). Some other researchers even reported comparable level of CO with H_2 for ethanol catalytic reforming [20, 37]. The results of experiments conducted by Terry Alger et al. [26] manifested that CO production was at least twice over that of H_2 in the gasoline in-cylinder reformed gases. James P. Szybist et al. [33] and Vickey B. Kalaskar et al. [34] found that the CO production was comparable to that of H_2 . In addition, they also discovered that CO and H_2 varied

from parent fuel and production of CO relative to H₂ is higher for higher molecular weight hydrocarbon fuels. Besides, the other minor components came into being, such as methane, ethylene, propylene and so on. Nevertheless, H₂ and CO are still the majority of the combustibles in the reformed gas.

Lei Zhu et al. [38] conducted in-cylinder fuel reforming experiments on a spark ignition natural gas engine, both significant amount of H₂ and CO were found in natural gas reformat and better engine performances were obtained compared with conventional EGR case. The influence of reformed gas on the engine is the results of the joint impact of each component in the reformed gas. A detailed knowledge of each component in reformed gas is essential for judging or making better use of the reformed gas as well as reforming technologies. However, the effects of the incombustible components (CO₂, N₂) in the reformed gas has been detailedly discussed in our previous studies [39]. The main goals of this paper are to evaluate the effects of CO and H₂ on natural gas engine performances and to disclose the reasons behind any improvement or degradation by CO and H₂. H₂ and CO both existed concurrently in the reformed gas and hence their blends are also tested in engine experiments to see their joint effects.

2, Experimental setup and methodology

In this research, experiments was carried out on a four-cylinder, water cooled, turbo-charged, four-stroke, spark ignition natural gas engine. The displacement volume of this engine was 5.3L and the compression ratio was 11. The specification of the test engine is shown in Table 1. An eddy current dynamometer was coupled to the engine for engine speed and torque control. The schematic diagram of this test system is shown in Fig 1. In this study, in-cylinder pressure of the

second cylinder was measured with Kistler piezoelectric transducer (type 6118BFD35 Q03A41) for combustion analysis. The resolution of the transducer was 10 Pa. After being amplified by Kistler charge amplifier (type 5015), cylinder pressure was supplied to combustion analyzer (D2T Evolution 3) along with crank angle signal and recorded by computer. The crank angle signal was generated by a 60-teeth gear with a single missing tooth and sensed by a magneto-electric tachometric transducer. CO emission was measured by non-dispersive infra-red analyzer (NIDR CAI 602P). Total hydrocarbon (THC) and NO_x emission were measured by hydrogen flame ionization detector (HFID CAI 600) and heat chemiluminescent analyzer (HCLD CAI 600) respectively. A self-developed procedure with Labview software was used for emission data acquisition.

In this study, natural gas was supplied through the natural gas injection assembly, on which six injectors (type: NGI2, 0280158830) were mounted, via a pressure reducer from CNG bottles. The amount of natural gas fuel was controlled by ECU and measured by a Micro Motion Coriolis natural gas mass flow meter (type: CMF025M319NWBZMZZZ). The main component of the natural gas used in this study was 96% methane with some other impurities as shown in Table 2. H₂, CO and their blends were injected by another set of injection assembly (type: NGI2, 0280158830) controlled by computer via a single chip and a controller according to the signal feedback from the natural gas mass flow meter. The injection assembly was originally designed for natural gas, while, it was recalibrated for H₂, CO and their blends for usage in this experiment. All these gases in this study were injected at intake manifold as Fig. 1 shows. Using Labview software, a self-developed procedure was used to control the ratio of H₂ and CO relative to natural gas.

In previously discussed investigations accomplished by other researchers, H_2 and CO from reformed gas in the engine intake could be up to about 1.8-2.5% [19, 20, 26, 38], which indicates roughly 18-25% mole percentage of H_2 and CO in whole engine fuel. In this paper, the volumetric (or molar) percentage of H_2 , CO or their blends in the engine fuel is taken as 20% in experiments.

Engine rotating speed was fixed at 1500rpm, and four loads, 3.05bar, 5.35bar, 7.65bar, 9.94bar were tested in this study. For all the tests, the spark ignition advance was fixed at 20 crank angle degree before top dead center (BTDC) and equivalence ratio was fixed at 0.73. Engine coolant and lubrication oil temperature were controlled to be 78~80°C and 80~85°C, respectively. All data were recorded when the engine running reached its steady state. Cylinder pressure was recorded every 0.5 crank angle degree and 200 consecutive cycles were saved and averaged to make combustion analysis.

Based on the first law of thermodynamics and ideal gas assumption, a zero dimensional model, which neglected the leakage through the piston ring and assumed specific heat of each intake component to be constant, was used to make combustion analysis. The details refer to our previous researches in [39].

3, Results and discussion

3.1 Effects of CO and H_2 on the in-cylinder combustion characteristics

To know the effects of CO and H_2 on affecting engine combustion and performances, in our experiments, either CO or H_2 was inducted into the intake pipe proportionally to natural gas flow. Besides, as H_2 and CO both existed concurrently in the reformed gas, their blends ($H_2(v):CO(v)=1:3, 1:1, 3:1$) were also tested to see their joint effects on engine. The volume

percentage of CO, H₂ or their blends in engine fuel was fixed at 20%.

As Fig. 2 shows, both H₂ and CO increase the peak of cylinder pressure and heat release rate. In addition, when H₂ or CO was inducted, heat release traces get more centralized and combustion phase was advanced, suggesting better in-cylinder combustion as well as higher engine effective thermal efficiency. In compare, H₂ is much more effective. With the increase of H₂ content in H₂-CO blends, a gradual and monotonous increase of both peaks of in-cylinder pressure and heat release rate is obtained as shown in Fig. 2.

Actually, in spark ignition engines, the laminar flame speed of the air-fuel mixture is an important factor that affects the engine combustion process and hence the engine performances. To reveal how CO and H₂ affect the combustion process and to disclose their similarities and differences, using Chemkin-Pro software with “premixed laminar flame speed” model based on USC Mech Version II [40], combustion kinetics of the fuel-air mixture were analyzed. Owing to the fact that CH₄ takes a very high proportion in NG fuel used in our experiments as shown in Table 2, CH₄ instead of NG was used in the simulation works. Laminar flame of CH₄, CH₄-CO, CH₄-H₂ and CH₄-H₂-CO blends were simulated. Standard condition, 298.15K and 101.32kPa, is selected as the initial condition for these simulation works. Equivalence ratio of unburnt reactants is set as 0.73, which is the same with engine operation condition.

During the oxidization process of hydrocarbon fuels, some elementary reactions and free radicals such as H, O, OH play significant roles due to their extremely high reactivity[41-43]. K. Yamamoto et al. [42] even found that a strong positive correlation between OH radical concentration and laminar flame speed. Results shown in Fig. 3 indicate that H, O and OH radical concentration increase evidently whenever CO or H₂ was added, which implies that either H₂ or

CO improves the chemical reaction process. This is verified by the heat release traces of the major reaction steps shown in Fig. 4 that almost all reactions are intensified when CO or H₂ is involved. Thus, ultimately, the laminar flame speed the fuel-air mixture is also increased when H₂ and CO were added as shown in Table 4. Actually, the laminar flame speed of CO is much lower than that of natural gas as shown in Table 3. This is mainly because of the lack of OH radical when CO is burnt in dry air and undergoes “dry” oxidation mainly through equation (3-1) and (3-2), while its oxidation divert to equation R99 listed in Table 5, which is much more rapid than its counterpart, when burnt in wet air due to the existence of OH radical [44]. Ultimately, the laminar flame speed of CO-CH₄ mixture is even higher than that of either CO or CH₄ as shown in Table 3 and 4.

However, to disclose the differences between CO and H₂ on affecting the combustion processes, their effects on increasing heat production of the primary reaction steps are compared in Fig. 5. Results shows that their differences primarily lie in R3 (OH+H₂⇌H+H₂O) and R31 (CO+OH ⇌CO₂+H), which are top accelerated reactions for H₂ and CO addition (marked by the red dash line rectangles), which also signifies that the combustion process is accelerated mainly through R3 by hydrogen addition while through R31 by CO addition. However, both R3 and R31 tend to increase H radical concentration as demonstrated in Fig. 3. So, when either H₂ or CO is added, increased H radical directly accelerated R1 and R16 hence remarkably increased O and OH radicals and further improved R35, R84, R88, R89 and R125. Finally, the whole chain branching reaction gets improved due to the increased radicals such as O, H and OH. Fig. 4 also shows that the axial distribution of R3 lies more advanced than R31 does. Therefore, it is more convenient for

H radical gained from R3 than from R31 to diffuse to the unburnt region. This should be the primary reason why H₂ enhances the other reaction steps more remarkable than CO does (note that nearly all other reaction axial distributions lied more advanced than R3 and R31). Besides, the fact that axial distribution of R3 lies more advanced than R31 also results in a more advanced H radical distribution for hydrogen addition compared with the case of CO shown in Fig. 3. All these result in a higher laminar flame speed of H₂ addition compared with CO addition case as shown in Table 4.

In this paper, flame development duration ($\Delta\theta_{fd}$) and rapid combustion duration ($\Delta\theta_{rd}$) are calculated through equation (3-1) and equation (3-2), respectively. The effect of H₂, CO and their blends on flame development duration and rapid combustion duration of natural gas engine is shown in Fig. 6 and Fig. 7. Both H₂ and CO shorten flame development duration and rapid combustion duration ignoring engine load conditions while CO exhibits a weaker effect in compare. All these would mainly be ascribed to the increased laminar flame speed when H₂ and CO were added. With the increase of H₂ percentage in the fuel, the laminar flame speed also increase as shown in Table 4 and hence accelerates the flame development and propagation process in engine cylinder, leading to intensified heat release rate and increased cylinder pressure traces during the combustion process. Moreover, both H₂ and CO tend to stabilize in-cylinder combustion process. As shown in Fig. 8, CovIMEP is evidently decreased when either H₂ or CO was involved, indicating a smoothed engine running. Again, it could be found that the effect of H₂ is stronger than that of CO.

$$\Delta\theta_{fd} = \theta_{10} - \theta_{ST} \quad (3-1)$$

$$\Delta\theta_{rd} = \theta_{90} - \theta_{10} \quad (3-2)$$

277

278 3.2 Effects of CO and H₂ on the engine emission and performances characteristics

279 The influence of H₂ and CO on engine THC emission character of natural gas engine is
280 depicted in Fig. 9. It could be found that both H₂ and CO tend to decrease engine THC emission.
281 This is mainly due to the following possible reasons: firstly, H₂ and CO are fuel free of
282 hydrocarbon, they partially substitute a portion of hydrocarbon fuel thus decreases the THC
283 emission from fuel source; besides, H₂ and CO involves into the fuel-air chemical reaction,
284 intensifies the oxidation of hydrocarbon fuel and hence lead to more complete combustion;
285 moreover, H₂ and CO increases the adiabatic flame temperature (as shown in Table 4), thus
286 attenuate the quenching layer and weaken crevice effect and hence reduce unburnt fuel fraction.
287 However, compared with H₂, CO is less effective in reducing THC emission as shown in Fig. 9.
288 This is mainly ascribed to less reactivity of CO compared with H₂, which has been demonstrated
289 previously according to their combustion chemistry characters. Therefore, bulk in-cylinder
290 temperature would be lower with higher CO content in the H₂-CO blends, which lead to heavier
291 quenching and crevice effect, resulting in higher THC emission.

292 Fig. 10 shows the effect of H₂ and CO on CO emission character of natural gas engine. CO
293 increases engine CO emission remarkably. When CO was inducted, except for incomplete
294 oxidization of hydrocarbon fuel, incomplete combustion of CO in the fuel due to quenching and
295 crevice effect is also a substantial source of CO emission. Compared with pure natural gas case,
296 CO emission almost doubled when 20% CO was added. With the addition of H₂, the chemical
297 reaction of hydrogen as well as the enhanced bulk in-cylinder temperature improved unburnt
298 hydrocarbon partial oxidization thus results in the increase of CO emission, which could be

confirmed by the corresponding decreases of THC emission when H_2 was added shown in Fig. 9. This is the reason why CO emission is slightly increased under lower BMEP. However, under higher BMEP, blow-by effect becomes distinct, increased cylinder pressure after the addition of H_2 contribute to exhaust a small portion of unburnt THC in crevice of cylinder wall-piston-piston ring into crank case instead of exhaust valve, leading to a lower THC emission as well as CO emission in the engine exhaust. Nevertheless, compared with CO, the influence of H_2 on engine CO emission is limited. So, with the increase of CO percentage in H_2 -CO blends, CO emission distinctively increases.

The influences of H_2 and CO on engine NO_x emission is shown in Fig. 11. Results indicate that either CO or H_2 increases NO_x emission obviously. The factors that dominate the formation of NO_x are high temperature, high oxygen concentration and long reaction duration. In this study, the key factor that affects NO_x formation should be in-cylinder temperature as engine runs under fixed equivalence ratio and engine speed. As previously discussed, adding CO and H_2 tend to increase the in-cylinder combustion temperature and hence facilitated the formation of thermal NO_x . However, as hydrogen is more reactive, so, it improves in-cylinder temperature more than CO does hence yield higher NO_x production. So, with the increase of H_2 in H_2 -CO blends, NO_x emission increases.

As Fig. 12 shows, the effective thermal efficiency is improved with addition of H_2 and CO irrespective of the load conditions. This is mainly due to the improved cylinder combustion process. As H_2 and CO centralize heat release traces thus help to increase degree of constant volume of the in-cylinder combustion process hence result in a better thermal efficiency. Compared with H_2 , CO is less effective in improving in-cylinder combustion. So, when CO

percentage increase in the H₂-CO blends increases, engine thermal efficiency decreases. In other words, hydrogen is more effective than carbon monoxide does in improving engine thermal efficiency.

4, Conclusions

Fuel reforming technology (onboard or in-cylinder fuel reforming) is promising for improving engine combustion, emission and performance characteristics. The main combustibles of the reformed gas are H₂ and CO. To know the effect of H₂, CO and H₂-CO blends on engine combustion, emission and performance, each of them was inducted at engine intake port with 20% volumetric percentage in the fuel of natural gas engine in the experiments. Meanwhile, laminar flame speed simulation of CH₄, CH₄-H₂-CO, CH₄-H₂ and CH₄-CO blends were conducted to make better understanding on fuel combustion kinetics. The following results are obtained:

1, Both H₂ and CO increase the peak of cylinder pressure and heat release rate and advance their phases. In addition, when H₂ or CO was inducted, heat release traces get more centralized. With the increase of H₂ content in H₂-CO blends, both the peaks of in-cylinder pressure and heat release rate increase.

2, Addition of H₂ and CO shortens flame development duration and rapid combustion duration. Besides, H₂ and CO also lower CovIMEP of the engine, indicating a smoothed engine operation. In compare, hydrogen is more effective than CO. With the increase of H₂ percentage in H₂-CO blends, flame development duration and rapid combustion duration as well as CovIMEP decreases.

3, Simulation results reveal that H₂ and CO addition enhanced the laminar flame speed of

natural gas and hence improves in-cylinder combustion. However, results manifested that their mechanisms are different. H_2 primarily accelerates R3 ($\text{OH} + \text{H}_2 \rightleftharpoons \text{H} + \text{H}_2\text{O}$) while CO mainly improves R31 ($\text{OH} + \text{CO} \rightleftharpoons \text{H} + \text{CO}_2$). In compare, H_2 is more effective in intensifying the chemical reaction of fuel-air mixture than CO. So, higher laminar flame speed is achieved with H_2 addition instead of CO addition.

4, Both H_2 and CO help to lower THC emission and enhancing engine effective thermal efficiency. With the increase of H_2 percentage in H_2 -CO blends, THC emission decreases. However, their effects on CO emission are different due to different mechanisms. Hydrogen addition slightly affects CO emission while carbon monoxide addition remarkably increases CO emission because of incomplete combustion (mainly by quenching and crevice effect). Both H_2 and CO addition worsen engine NO_x emission while improve engine thermal efficiency.

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484 Table 1. Engine specifications

Number of cylinders	4	Bore	114mm
Number of strokes	4	IVO	22.5 CAD BTDC
Compression ratio	11	IVC	34.5 CAD ABDC
Displacement volume	5.3L	EVO	67.5 CAD BBDC
Connecting rod length	130mm	EVC	25.5 CAD ATDC

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487 Table 2. Composition of natural gas used in this study

Components	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	CO ₂	others
Volumetric percentage	96.04	2.58	0.56	0.23	0.41	0.18

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490 Table 3. Fuel properties of H₂, CO and NG

Properties	H ₂	CO	NG
Lower calorific value (MJ/Nm ³)	10.8[45]	12.63[45]	35.88
Flamability (%vol. of fuel in air)	4.1-75[19]	12.5-74.6[19]	5.0-15.0
Laminar flame speed (1atm, $\Phi=1.00$)	207.04[46]	16.52[46]	38.63
293.15K, cm/s) $\Phi=0.73$	153.49[46]	14.04[46]	-
Stoichiometric volume occupation in cylinder (%)	29.58	29.58	9.5
Stoichiometric mixture energy density (MJ/Nm ³)	3.19	3.74	3.41
Auto ignition temperature (K)	858[47]	882[47]	813[48]
Adiabatic flame temperature (K)	2380	2383	2220[48]

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493 Table 4. Calculated laminar flame speed and adiabatic flame temperature of different fuel air
494 mixtures. (equivalence ratio: 0.73, pressure: 101.325kPa, temperature: 298.15K)

Fuel composition (CH ₄ :H ₂ :CO)	100:00:00	80:00:20	80:05:15	80:10:10	80:15:05	80:20:00
Laminar flame speed(cm/s)	23.22	24.76	25.16	25.54	25.95	26.36
Adiabatic flame temperature(K)	1794.84	1803.3	1803.43	1803.49	1803.8	1804.07

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497 Table 5. Major reaction steps of CH₄-air mixture summarization

Reaction number	Reaction step
R1	$\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$
R3	$\text{OH} + \text{H}_2 \rightleftharpoons \text{H} + \text{H}_2\text{O}$
R16	$\text{HO}_2 + \text{H} \rightleftharpoons 2\text{OH}$
R31	$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$
R35	$\text{HCO} + \text{H} \rightleftharpoons \text{CO} + \text{H}_2$
R39	$\text{HCO} + \text{M} \rightleftharpoons \text{CO} + \text{H} + \text{M}$
R40	$\text{HCO} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H} + \text{H}_2\text{O}$
R41	$\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$
R59	$\text{CH}_2 + \text{O}_2 \rightleftharpoons \text{HCO} + \text{OH}$
R74	$\text{CH}_2^* + \text{O}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$
R84	$\text{CH}_2\text{O} + \text{OH} \rightleftharpoons \text{HCO} + \text{H}_2\text{O}$
R88	$\text{CH}_3 + \text{H} (+\text{M}) \rightleftharpoons \text{CH}_4 (+\text{M})$
R89	$\text{CH}_3 + \text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{H}$
R104	$2\text{CH}_3 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_6 (+\text{M})$
R125	$\text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$

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500 **Figure Captions:**

501 Fig. 1 The schematic layout of the experimental setup.

502 Fig. 2 Cylinder pressure and heat release traces along with crank angle.

503 Fig. 3 Computed axial distribution of H, OH, O radical concentration and net heat production rate
504 (equivalence ratio: 0.73, unburnt gas temperature: 298.15K, pressure: 101.325kPa).

505 Fig. 4 Computed axial distribution heat production rate of primary reaction steps (equivalence
506 ratio: 0.73, unburnt gas temperature: 298.15K, pressure: 101.325kPa).

507 Fig. 5 Increase of the peak of NHPR of the major reaction steps of CH₄ laminar flame after H₂ or
508 CO addition (equivalence ratio: 0.73, unburnt gas temperature: 298.15K, pressure: 101.325kPa).

509 Fig. 6 The effects of H₂, CO and their blends on flame development duration.

510 Fig. 7 The effects of H₂, CO and their blends on rapid combustion duration.

511 Fig. 8 The effects of H₂, CO and their blends on CovIMEP.

512 Fig. 9 The effects of H₂, CO and their blends on engine HC emission.

513 Fig. 10 The effects of H₂, CO and their blends on engine CO emission.

514 Fig. 11 The effects of H₂, CO and their blends on engine NO_x emission.

515 Fig. 12 The effects of H₂, CO and their blends on effective thermal efficiency.

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