Combustion and Flame 172 (2016) 94–104

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

# Effects of CO-to-$H_2$ ratio and diluents on ignition properties of syngas examined by weak flames in a micro flow reactor with a controlled temperature profile

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ARTICLE INFO

*Article history:*
Received 1 March 2016
Revised 18 April 2016
Accepted 22 June 2016

*Keywords:*
Syngas
Hydrogen
Carbon monoxide
Diluents
third-body reactions
Microcombustion
Advanced humid air turbine (AHAT)
Integrated gasification combined cycle (IGCC)

ABSTRACT

Weak flame positions at various CO-to-$H_2$ ratios in syngas combustion were investigated for stoichiometoric fuel ($CO/H_2$) and oxidizer ($O_2/N_2$) mixtures at 1:7 $O_2$:$N_2$ using a micro flow reactor with a controlled temperature profile. In the case of low $H_2$ mole fractions in fuel (0–10%), the experimental weak flame position significantly shifted to the lower temperature region with the increase of the $H_2$ mole fraction in fuel, and this trend was well reproduced by the computations with all reaction mechanisms employed (GRI Mech. 3.0, San Diego Mechanism, Princeton C1 Model, AramcoMech 1.3). The reactivity of the syngas strongly depended on the variation of the CO-to-$H_2$ ratio, in the case of higher $H_2$ mole fractions in fuel (25–100%), on the other hand, the experimental weak flame position was almost insensitive to the CO-to-$H_2$ ratio. This trend was well reproduced by the computations except GRI Mech. 3.0 among the above reaction mechanisms.

Weak flame positions for three kinds of diluents ($N_2$, $CO_2$ and $H_2O$) and their molar fractions in fuel were also investigated for stoichiometoric fuel ($CO/H_2$/Diluent) and oxidizer ($O_2/N_2$) mixtures at 21:79 $O_2$:$N_2$ (equivalent to air). The diluent fraction in fuel varied up to 50% (mole fraction of 0.228 in a mixture). Only in $H_2O$ dilution among these three diluents, the experimental weak flame position shifted to the higher temperature region with the increase of the diluent fraction. The chemical inhibition of reactivity by the $H_2O$ dilution was observed in the present micro flow reactor. Rate of production and reaction-pathway analyses by San Diego Mechanism revealed that the higher $H_2O$ mole fraction enhanced R10: $H+O_2(+M)=HO_2(+M)$ and R16: $2OH(+M)=H_2O_2(+M)$ because of higher third-body efficiency of $H_2O$. The similar inhibition mechanism by an increase of pressure is extensively known in the mild ignition regime of the general $H_2$–$O_2$ explosion peninsula. An analogy between the inhibition mechanisms by the increases of pressure and $H_2O$ concentration was discussed. The chemical inhibition by $H_2O$ dilution was considered to be found due to the unique characteristic of the present micro flow reactor which allows to evaluate the reactivity of a given mixture in the thermally-equal condition independent of diluent thermal properties.



## 1. Introduction

Integrated Gasification Combined Cycle (IGCC) is one of the promising technologies to reduce $CO_2$ emission from power plants operated with coal as fuels. Instead of direct combustion of coal in boilers, synthesized gas (syngas) is generated by the gasification of coal and is employed in a combined cycle. Main combustible components of syngas are $H_2$ and CO and main diluent components of syngas are $N_2$, $CO_2$ and $H_2O$. The CO-to-$H_2$ ratio and the diluent fraction in syngas widely vary depending on types of coal and gasification methods [1–4]. For future high-efficiency closed-cycle Integrated coal Gasification Advanced Humid Air Turbine (IG-AHAT) system [5,6], gas turbine combustors need to be flexibly designed and developed for various syngas/diluent mixtures. Therefore, fundamental combustion characteristics of syngas over a wide range of the CO-to-$H_2$ ratio and the diluent fraction must be investigated.

Extensive experiments have been made to obtain fundamental combustion characteristics of syngas so far. Flame speed

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http://dx.doi.org/10.1016/j.combustflame.2016.06.024
0010-2180/

measurements for $CO/H_2$/air mixtures have been conducted over a wide range of the CO-to-$H_2$ ratio [7–9]. Effects of the diluent fraction on flame speeds have been also studied for $N_2$ [10], $CO_2$ [11–14] and $H_2O$ [15,16] dilutions. Recently, importance of ignition characteristics for the stabilization of turbulent premixed jet flames was examined [17] and it is emphasized that not only flame characteristics but also ignition characteristics need to be studied. Shock tube experiments have been widely conducted to measure ignition delay times for $CO/H_2/O_2$/Ar [18–20] as well as $CO/H_2$/air mixtures [21,22]. Rapid compression machines have been employed to obtain ignition delay times of $CO/H_2$ at relatively lower temperature conditions [23–26]. Effects of $CO_2$ [27] and $H_2O$ [28–30] dilutions on $CO/H_2$ ignition have been studied. These fundamental data have been utilized for validation and development of syngas reaction mechanisms [31–36].

To further investigate fundamental ignition characteristics of syngas over a wide range of the CO-to-$H_2$ ratio and the diluent fraction, weak flames in a micro flow reactor with a controlled temperature profile [37,38] were employed in this study. It is because the observation and analysis of weak flame in the present micro flow reactor enable to examine ignition properties of test fuels and are applicable to low reactivity fuels like CO as described below in detail. A quartz tube with an inner diameter smaller than the quenching diameter is employed as a reactor channel and heated by an external heat source to form a stable temperature gradient along the flow direction on the inner wall surface. A test mixture is supplied to the reactor from the lower temperature side and stable weak flames are observed in the very low flow velocity condition. The theoretical analysis [39] has shown that weak flames in the micro flow reactor represent ignition characteristics of a test mixture based on the fact that the weak flame branch is on the ignition branch of the Fendell curve. Since the gas-phase temperature profile is strongly governed by the given wall-temperature profile due to the significant heat transfer in a narrow channel and small chemical input energy in the low flow velocity condition (typically less than 1 W), rapid temperature increase due to the heat release is suppressed and temperature difference between gas and wall is extremely small even at the reaction zone (typically less than 10 K). Therefore, weak flame represents initiation of ignition prior to thermal runaway. In general, ignition is a transient phenomenon with a quite short time scale while the weak flame represents initiation of ignition as a steady phenomenon. Two-stage ignition processes of higher hydrocarbons have been reproduced as steady, multi-stage oxidation processes (steady, spatially-separated multiple weak flames) in the micro flow reactor [40–43]. Wall temperature at the weak flame position is considered to be a representative temperature of corresponding oxidation. Thus, fuel reactivities have been measured by observing the responses of the weak flame position. The weak flame positions have shifted to higher temperature region with an increase of octane number for gasoline primary reference fuels [42] and natural gas components [44]. The same trend has been observed with a decrease of cetane number for diesel primary reference fuels [43]. The capabilities of the micro flow reactor to investigate the reactivity and the ignition of a given mixture have been demonstrated from these past studies. As a notable characteristic, the micro flow reactor is capable to examine extremely low reactivity mixtures such as pure CO or highly-diluted mixtures because of the long residence time in the heat-loss compensation nature of the system. Therefore, the micro flow reactor is expected to provide detailed information of the syngas reactivity and its ignition properties under the thermally-equal condition over a wide range of the CO-to-$H_2$ ratio and the diluent fraction.

The objective of this study is to investigate fundamental ignition and combustion characteristics of syngas over a wide range of the CO-to-$H_2$ ratio and the diluent fraction using weak flames in the micro flow reactor with a controlled temperature profile. Experiments and computations with detailed reaction mechanisms were conducted for fuel ($CO/H_2$) and oxidizer ($O_2/N_2$) mixtures at various CO-to-$H_2$ ratios and effects of the CO-to-$H_2$ ratio on weak flame positions were examined. In addition, $N_2$, $CO_2$ and $H_2O$ were employed as diluents of fuels and effects of diluents and their molar fractions on weak flames positions were examined.

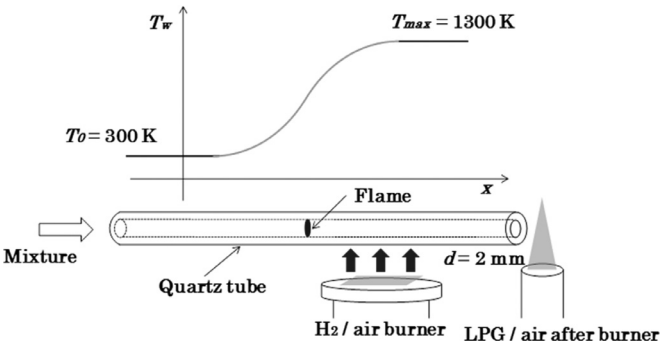


**Fig. 1.** Schematic of experimental setup.

## 2. Experimental setup

Figure 1 shows a schematic of the experimental setup. A quartz tube with an inner diameter of 2 mm was used as a reactor channel. A hydrogen/air flat-flame burner was employed as an external heat source and the stationary temperature profile from ambient temperature to 1300 K was formed along the inner surface of the reactor channel, as shown in Fig. 1. Hereafter, "wall temperature" means temperature on the inner surface of the reactor. The wall-temperature profile in the axial direction was measured using a K-type thermocouple (diameter of 0.25 mm) inserted from the exit of the reactor. The overall measurement error was estimated to be smaller than 10 K. The details of the temperature measurement can be found in [43].

Two kinds of effects on syngas weak flames were investigated in this study: (1) CO-to-$H_2$ ratio effect and (2) diluent effect. Experimental conditions in the investigations of both effects are summarized in Table 1. In the investigation of the effect of CO-to-$H_2$ ratio on syngas weak flames, fuel ($CO/H_2$) and oxidizer ($O_2/N_2$) mixtures were supplied to the reactor at various CO-to-$H_2$ ratios. To avoid flash back in cases of higher $H_2$ mole fractions (low CO mole fractions), the 1:7 $O_2$-to-$N_2$ ratio was employed for all CO-to-$H_2$ ratios. The purities of all the gases were higher than 99.995%. Flow rates of the gases were controlled by mass flow controllers. In the investigation of the diluent effect, the CO-to-$H_2$ ratio was fixed at 50:50. The $O_2$-to-$N_2$ ratio was fixed at 21:79, which is the same ratio as air. Three types of diluents, $N_2$, $CO_2$ and $H_2O$, were employed in this study. Each diluent was considered as contained in fuel and the diluent fraction in fuel, $F_d$ = Diluent / ($CO + H_2$ + Diluent), was set at 0%, 25% and 50%. Mole fractions of CO, $H_2$, $O_2$, $N_2$ and diluent at $F_d$ = 0%, 25% and 50% were summarized in Table 2. In the case of $H_2O$ diluent, the liquid $H_2O$ was supplied into preheated $CO/H_2/O_2/N_2$ mixture flow using a micro-syringe with a prevaporizer and gaseous $H_2O$ was mixed into the $CO/H_2/O_2/N_2$ flow. The micro-syringe was installed in a stage and rate of the $H_2O$ supply was controlled using a stepping motor by changing the displacement of the stage. The $CO/H_2/O_2/N_2$ mixture flow was preheated at 373 K by an electric heater which covered the upstream region of the flow reactor channel. Note that this method was successfully used for supplying gaseous $C_{16}H_{34}$/air mixtures to the reactor in the previous study [43]. Distilled water was used as $H_2O$. All experiments were conducted at atmospheric pressure and