

Full Length Article

Micro-Explosion mechanism of iron hybrid Methane-Air premixed flames

Yueh-Heng Li^{a,b,*}, Aris Purwanto^a, Bo-Cheng Chuang^a^a Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan, ROC^b International Bachelor Degree Program on Energy Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC

ARTICLE INFO

Keywords:

Hybrid flames
Iron particles
Metal combustion
Micro-explosion

ABSTRACT

Compared to gaseous hydrocarbon flame, a metal hybrid flame has higher energy and even has a higher flame temperature. This study explored the micro-explosion mechanisms of iron particles in methane-air premixed flames. Four different particle sizes were used in this experiment, that is 2–10 μm , 50 μm , 100 μm , and 150 μm . A conical methane-air premixed flame was fixed in a stoichiometric condition and doped with iron particles at various feeding rates. The 50- and 100- μm iron particles had a 20% and 500% higher micro-explosion probability than the 2–10- μm particles. The micro-explosion probability would increase with the increase of particle size. In addition, the micro-explosion probability of the 2–10 μm iron particles was 125% higher under 10% CO addition than under no CO addition. CO plays a critical role in increasing the micro-explosion probability of iron particles smaller than 50 μm .

Regarding the mechanism of the micro-explosion of iron particles, the oxidizer diffuses into iron particles and produces iron oxide in a thin shell. However, limited oxygen heterogeneously reacts over the surface of the iron particles and produces Fe_3O_4 . Fe_3O_4 comprises FeO and Fe_2O_3 . However, when CO reacts Fe_3O_4 , this reaction makes Fe_3O_4 redox into fresh Fe particles, whereas it will lead to FeO while Fe reacts with O_2 predominantly. The presence of FeO brings about iron particles blinking and shrinking right after passing the flame front. When CO was dominated in the reaction, it gave rise to the formation of $\text{Fe}(\text{CO})_5$ gas bubbles in the film of iron particles. During the agglomeration of the bubbles, incorporating $\text{Fe}(\text{CO})_5$, CO, O_2 , and N_2 , the iron particles expand gradually and become hollow spherical particles eventually. However, under special conditions, this particle expansion will deteriorate the micro-explosion of the iron particles.

1. Introduction

In general, metal powders possess a high energy density and a wide application in explosive, propellant, and pyrotechnics. Especially, micron-sized iron powder features a good industrial foundation, low preparation cost, nontoxic safety, easy storage, and transportation. Micron-sized iron particles are expected to burn heterogeneously, and the flame temperature of iron/air suspensions is approximate 1800 ~ 2200 K, which is comparable to that of hydrocarbon fuels [1]. The combustion characteristics of micron-sized iron powder in hydrocarbon/air flames were examined in all aspects, such as flame structures [2,3], flame propagation and quenching properties [4], and flame temperatures [5,6].

Interestingly, the combustion of micron-sized iron powder in hydrocarbon/air flames is prone to induce the micro-explosion behavior, indicating the nonlinear change of iron particle trajectory and the formation of smaller fragments. Poletaev and Khlebnikova [7] studied the

iron particle micro-explosion in laminar and diffusion flames and concluded that the intensity of micro-explosions of iron particles is associated with metal mass concentrations in air. Li *et al.* [8] examined the combustion characteristics of pure iron and iron cofiring with aluminum and coal particles, respectively. They speculated that the resulting CO gas from the thermal pyrolysis of coal particles is trapped inside the molten iron shell and yields combustible iron pentacarbonyl ($\text{Fe}(\text{CO})_5$). The coalescence of $\text{Fe}(\text{CO})_5$ and O_2 expedites bubble growth, even inducing the micro-explosion of iron particles. Huang *et al.* [9] scrutinized the micro-explosion of burning iron particles in different oxidizing environments. They concluded that the occurrence of micro-explosion is affiliated with the surrounding gas temperature and oxygen concentration. Ning *et al.* [10] inspected a single iron particle burned in O_2/N_2 mixture with oxygen content varying from 21% to 36%. Reportedly, the combustion regime and burning time of laser-ignited single iron particle manifested that the overall combustion process of iron combustion is dominated by external diffusive of oxygen

* Corresponding author.

E-mail address: yueheng@mail.ncku.edu.tw (Y.-H. Li).<https://doi.org/10.1016/j.fuel.2022.124841>

Received 2 May 2022; Received in revised form 5 June 2022; Accepted 8 June 2022

Available online 15 June 2022

0016-2361/© 2022 Elsevier Ltd. All rights reserved.

and then the internal diffusive of oxygen due to the oxygen saturation on the particle surface. In addition, Ning *et al.* [11] employed a two-color pyrometer to gauge the time-resolved particle temperature and estimated melting time. Besides, an abrupt brightness jump near the end of combustion is attributed to the sudden crystallization of a supercooled iron oxide droplet with oxygen content close to Fe_3O_4 or higher. However, the micro-explosion behavior can be inspected in other metal particles, including Zr, Al, and Ti [12–15]. For example, Badiola *et al.* [13] observed the micro-explosion in the combustion of Ti – Zr powders, and the resulting debris of the micro-explosion experienced a secondary micro-explosion. Wainwright *et al.* [14,15] observed bubbling and micro-explosions in ball mill Al–Zr powder in wire combustion in different oxidizer conditions. They assumed that the metal powder with fast bubble growth would trigger the micro-explosion, and particles with slow bubble growth would only expand the oxide shell on the core (bubbling). However, the proposed internal mechanism of gas release, bubble nucleation, and bubble growth to describe the external mechanism of micro-explosions has implemented to interpret the micro-explosion of fuel droplet [16,17].

In this study, we explored the micro-explosion mechanisms of iron particles in methane – air premixed flames. Additionally, iron has unique modes of heterogenous and homogenous combustion. Moreover, different sizes of iron particles have different combustion traits, burning speeds, and thermal stabilities [1]. This study also observed that the combustion product of iron particles, i.e., Fe_2O_3 and Fe_3O_4 , superseded the iron particles in hybrid methane premixed flames to examine if causing the micro-explosion of the iron particles.

2. Experimental apparatus

Four samples of iron particles of different sizes, supplied by Sichuan Zichuan New Material China supplied, were used: iron 2–10- μm , 50- μm , 100- μm , and 150- μm , respectively. According to chemical analysis, the purity of the iron particles was greater than 98%, and the carbon content was less than 0.03%. Generally, smaller particles have a larger surface-area-to-volume (S/A) ratio, affecting the reaction and burning rates. The solid particles with sizes of less than 30 μm burn like gas fuels [1]. In addition, two different iron oxide particles were also selected to compare their combustion behaviors in methane – air premixed flames. Two solid iron oxide particles are Fe_3O_4 and Fe_2O_3 , respectively, used to examine if they are intermediate species to trigger particle micro-explosions. Their particle sizes are 2–10 μm , and the purity of both iron oxides is greater than 99%. Iron particles of four sizes have an irregular shape before combustion. Fig. 1 shows the SEM photographs of pure Fe, Fe_3O_4 , and Fe_2O_3 with sizes of 2–10 μm .

Fig. 2 depicts the experimental apparatus and the corresponding measurement systems. A stainless-steel jet burner with the inner diameter and the nozzle height of 11.5 and 120 mm was employed in this study. Methane – air equivalent ratio was fixed at a stoichiometric value. To examine the effect of CO presence on micro-explosions of iron

particles, CO with a purity of 99.5% was employed in this experiment. CO concentrations were diluted with 1%, 5%, and 10% fuel volume fraction. To supply iron particles to the burner with a stable mass flow rate, a low-concentration particle disperser (RBG 1000, Palas GmbH Aerosol Technology, Germany) was used for delivering metal particles into the jet flames. The detailed information on the burner and aerosol generator can be found in the previous study [8].

Flame images were captured with a Digital Single Lens Reflection camera (DSLR) for each particle size. Additionally, the high-speed camera (Photron SA-X, Photron Limited, Tokyo, Japan) was used to observe the particle trajectory and micro-explosion of a metal particle in hybrid flames. In addition, a self-locked stainless-steel tweezer with a 0.2-mm wide tip was combined with a double-acting air actuator to capture the solid product with a copper foil plate (1 mm in diameter). The sieved sample was analyzed using an SEM–EDS device (Hitachi S-4800, Hitachi, Tokyo, Japan).

3. Results and discussion

3.1. Thermogravimetric analysis

A thermogravimetric analyzer (TA-SDT Q600, TA Instruments, New Castle, DE, USA) was used to perform the preliminary result to understand the oxidation stage of solid particles and calculate the solid oxide product of iron particles. Each fuel was heated up to 1273 K, and the heating rate and oxidizer flow rate were 10 K/min and 60 mL/min, respectively. Two different gas environments are air condition (21% O_2 and 79% N_2) and air with CO addition (11% O_2 , 10% CO, and 79% N_2), respectively. For each particle, the oxidation temperature was defined as the temperature at which particles reach maximum mass gain, similar to theoretical gain. Some studies used TGA to observe the thermal stability and mass gain or loss of metal [18–21] or coal particles [8,30,31]. Fig. 3 – Fig. 5 show the single-step oxidation process of Fe, Fe_3O_4 , and Fe_2O_3 particles in different oxidation environments.

In Fig. 3, Fe particles started to gain weight at a temperature of 424 K. When the temperature reached 940 K, iron particles reached an oxidation peak, and the mass increased at this peak was found at 41.8%. It assumed that iron particles were turned into Fe_2O_3 [22]. Fe was oxidized through the formation of an intermediate product through the following process: $\text{Fe} \rightarrow \text{FeO} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$. Notably, the mass gain percentage of Fe also corresponded with the theoretical value of 43%. And the oxidation stage kept plateau until the temperature reached 1273 K. For CO cases, the momentum of mass increment in iron particles remained until the temperature of 1000 K. After then, a total mass gain of iron particles achieved 37.95%. This mass gain is attributed by iron particles converting into Fe_3O_4 particles. This mass gain is similar to the theoretical mass gain of Fe to Fe_3O_4 , which has a 38% mass gain value. When iron particles react with CO, iron particles are not converted into Fe_2O_3 but Fe_3O_4 .

In Fig. 4, when Fe_3O_4 particles were heated in an air environment,

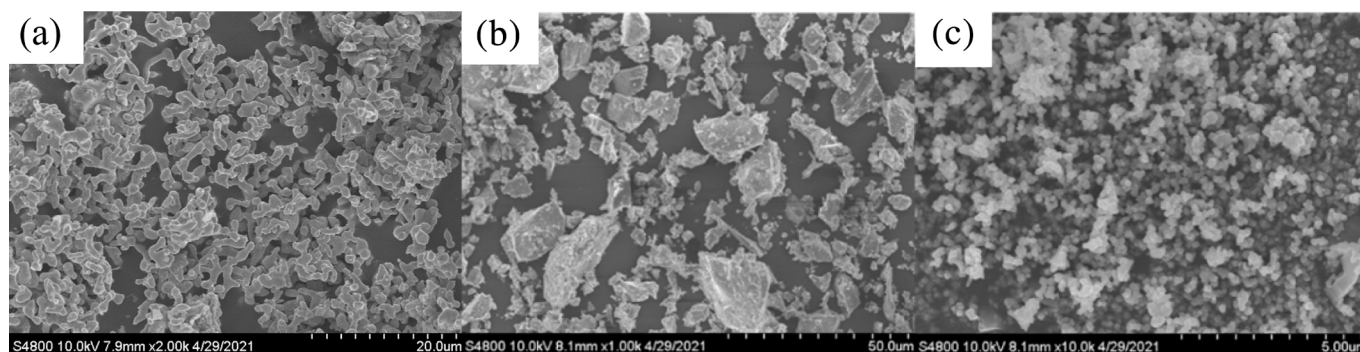


Fig. 1. SEM images of (a) Fe particle, (b) Fe_3O_4 , and (c) Fe_2O_3 with the size of 2–10 μm .

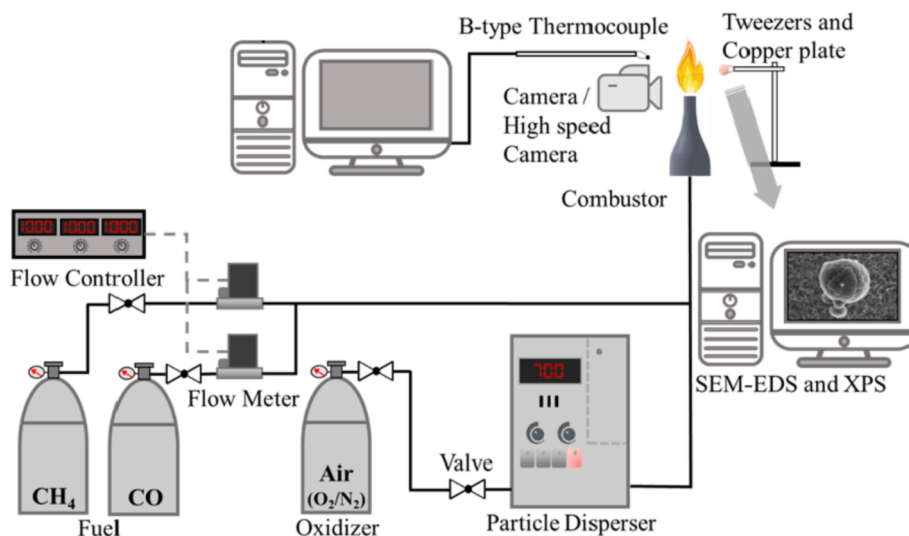


Fig. 2. Experimental apparatus and measurement system.

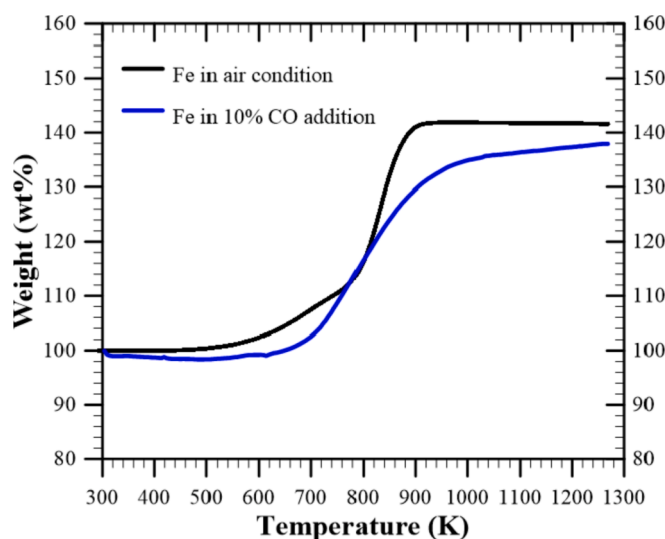
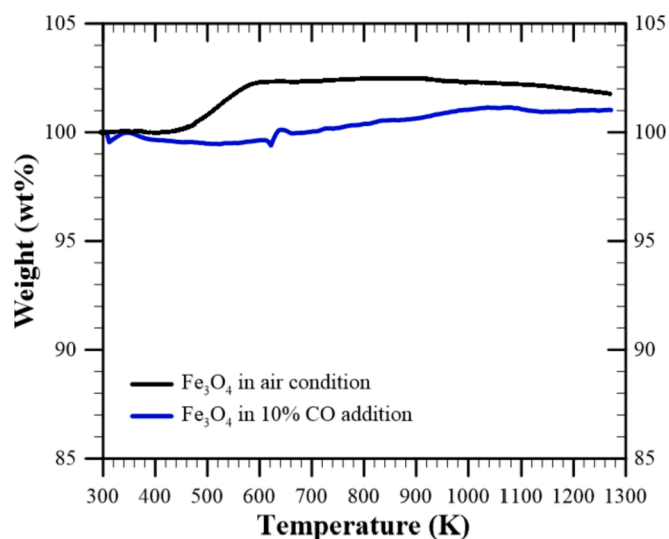


Fig. 3. Thermogravimetric curves for (a) Fe in air condition and (b) Fe in 10% CO addition in air.

particles started to gain mass from 450 to 600 K. When the temperature was higher than 600 K, Fe_3O_4 gained 3% in mass, and this mass gain remained until 1273 K. These mass gain of Fe_3O_4 particles represented that Fe_3O_4 was transformed into Fe_2O_3 particles. When Fe_3O_4 particles were heated in the case of CO addition, particles would reduce their mass before the temperature reached 600 K. When Fe_3O_4 particles reached a temperature of 600 K, the mass slightly increased. However, this increase in mass was not substantial. At the temperature of 1273 K, Fe_3O_4 particles only increased 1.03 % in mass. The results of this experiment demonstrate that CO is not favorable to reacting with Fe_3O_4 .

Fig. 5 demonstrates that Fe_2O_3 gradually decreases in mass from 300 to 1273 K in the air environment. Principally, Fe_2O_3 particles partially decomposed and converted to Fe_3O_4 particles. There was a 4% mass decrease at the temperature of 1272 K. However, the mass of Fe_2O_3 particles gradually decreased in the CO condition. The decreasing rate was similar to the case in the air condition until the temperature of 1000 K. It is noted that the mass of Fe_2O_3 particles apparently decreased to 88.33% at the temperature of 1000–1100 K, equivalent to the theoretical mass gain of Fe_2O_3 to Fe_3O_4 which has 88.87% mass gain value. It concludes that Fe_2O_3 particles are prone to decompose into Fe_3O_4

Fig. 4. Thermogravimetric curves for (a) Fe_3O_4 in air condition and (b) Fe_3O_4 in 10% CO addition in air.

particles in the CO-adding environment; that is, CO reacts more easily with Fe_3O_4 at high temperatures.

3.2. Particles shape morphology and chemical composition

The particle transformation of hybrid flames at three heights above the burner (HAB), namely 10-, 30-, and 60-mm, is shown in Fig. 6. Particles captured at a HAB of 10 mm (inside the flame cone) are still in irregular shape, which indicates that the iron particles are subjected to incomplete reactions. Moreover, the aforementioned observation indicated that at a HAB of 10 mm, some iron particles did not complete their shape transformation and did not expand because of the relatively low temperature inside the flame cone. At a HAB of 30 mm, iron particles were turned into spherical shapes because iron particles reacted with the product gases (CO , CO_2 , O_2 , and N_2) of methane – air combustion after passing the flame front. These reactions resulted in the formation of iron particles with a semispherical or oval shape. The iron particles captured at a HAB of 60 mm were smooth and spherical, and these particles were larger than those found at a HAB of 30 mm.

The captured particles were analyzed through energy-dispersive X-

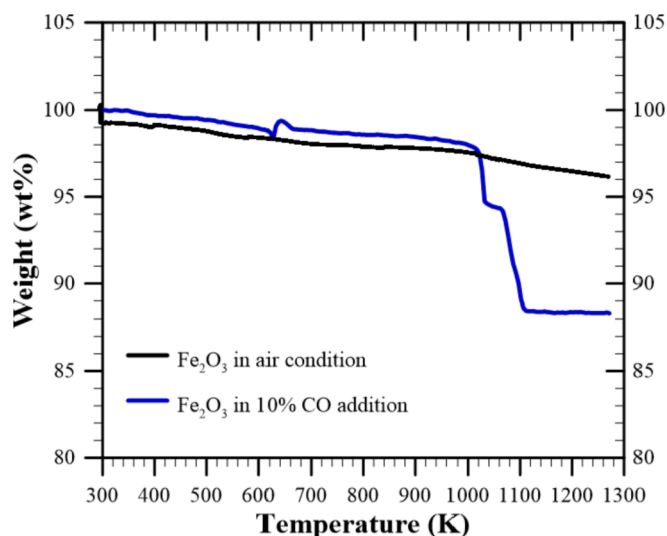


Fig. 5. Thermogravimetric curves for (a) Fe_2O_3 in air and (b) Fe_2O_3 in 10% CO addition in air.

ray spectroscopy (EDS, S – 4800, Hitachi, Tokyo, Japan) and electron spectroscopy for chemical analysis (ESCA, PHI 5000 VersaProbe, ULVAC-PHI Inc., Kanagawa, Japan). A HAB of 30 mm was selected for EDS analysis, and the results indicated that the 2–10- μm iron particles contained 43% iron and absorbed 33% oxygen and 24% carbon. The 2–10- μm iron particles absorbed more carbon than the iron particles of other sizes. At a HAB of 60 mm, the results indicated that iron particles contained more oxygen at a HAB of 60 mm than at a HAB of 30 mm because they could react with environmental oxygen more easily at a HAB of 60 mm.

3.3. Iron particles Micro-explosion

A micro-explosion is a unique combustion behavior of metal particles. Micro-explosions have been observed in the combustion of aluminum and zirconium [14,15] and the combustion of aluminum – magnesium mixed particles [23]. Furthermore, a micro-explosion phenomenon was also observed in mixed Fe-coal mixed particles in hybrid flames [8]. Micro-explosions and primary, secondary, and tertiary explosions were observed in mixed iron-coal particles in hybrid flames. To investigate the micro-explosion process of hybrid flames, a high-speed camera was used in the present study to record the combustion behavior of burning iron particles. The feeding rate for the hybrid iron premixed flames varied from 58.28 g/m^3 , 61.28 g/m^3 , 62.93 g/m^3 , and 81.01 g/m^3 . The frame rate of the high-speed camera was set as 30,000

frames per second. Fig. 7 (a) presents the images obtained for 2–10- μm iron particles. These images show micro-explosions during the time interval of 0.0531 s in the post-flame zone. It appears that the particle size obviously grows within 0.0519 s and then induces micro-explosion and fragmentation at a time of 0.0531 s. Similarly, Fig. 7 (b) and 7 (c) display the images obtained using the high-speed camera for 50- μm and 100- μm iron particles, respectively. These images exhibited micro-explosions in the time interval of 0.0391 s and 0.0177 s. In summary, Fig. 7 (a) – (c) demonstrate that before iron particles explode, iron particles expand, and due to an increase in pressure inside the particles, the particle shells are unable to withstand the pressure, so the particles abruptly explode. The videos taken by the high-speed camera are shown in the supplementary files (file name: Fe2-10, Fe50, Fe100 for the case of 2–10- μm , 50- μm , and 100- μm iron particles, respectively).

3.4. Iron particles 2–10 μm with CO addition

Combustion of iron particles with different sizes of particles was discussed. Particularly, iron particles with 2–10 μm have a lower probability of micro-explosion. CO is speculated to be the precursor that initiates particle micro-explosion in a hybrid iron premixed flame. To prove the aforementioned speculation, there are three conditions of CO addition, namely 1%, 5%, and 10% CO replacement in fuel, in hybrid iron-methane-air flames.

An experiment was conducted in which CO gas was used to replace methane gas partially, and the air was used to transport iron particles into the burner nozzle. The particle feeding rates were 58.30, 116.60, and 163.20 g/m^3 . The flame structure was observed using a DSLR camera under identical settings and parameters (ISO 1000, exposure time of 1/50 s, aperture of f10, DC HSM 30 mm f1.4 lens). Observations of particle trajectories were made using the high-speed camera mentioned. Under the addition of low CO concentration (1% of CO addition), minor micro-explosions were observed. At some critical concentrations, the presence of CO enhances the probability of iron particle micro-explosion. A higher CO concentration (5% or 10% of CO addition) results in a significantly higher probability of iron particle micro-explosion, as shown in Fig. 8. CO is prone to bond chemically with iron within the flame sheet. Moreover, CO becomes trapped inside iron particles when their shape changes from irregular to spherical. The CO may then cause the formation of $\text{Fe}(\text{CO})_5$ inside spherical iron particles, initiating their micro-explosion.

Table 1 (a) presents the number of micro-explosions exhibited by iron particles without CO of various sizes within 0.65 s – 4, 6, and 24 micro-explosions for the 2–10-, 50-, and 100- μm iron particles, respectively. The 50- and 100- μm iron particles had a 20% and 500% higher micro-explosion probability than the 2–10- μm particles. The results indicate that when the particle size was increased, the probability of micro-explosion also increased. Iron particles smaller than 50 μm had a

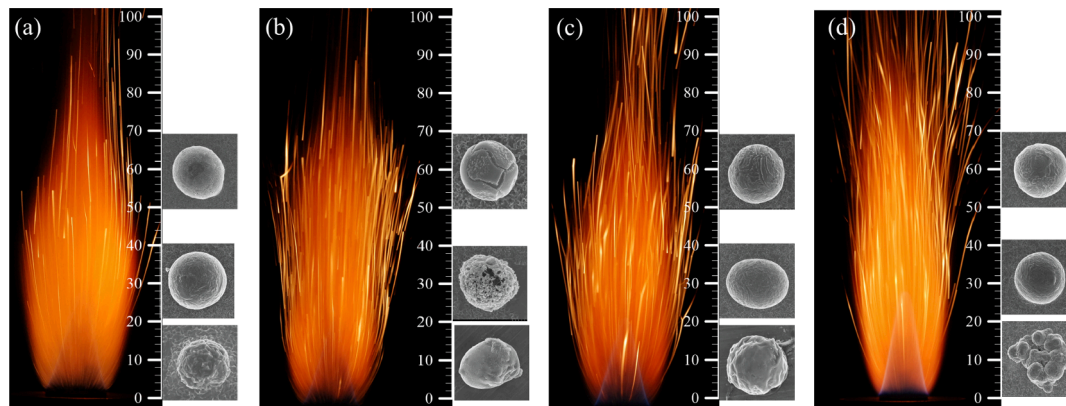


Fig. 6. The iron product transformation at various positions of (a) iron 2–10 μm case, (b) iron 50 μm case, (c) iron 100 μm case, and (d) iron 150 μm case.

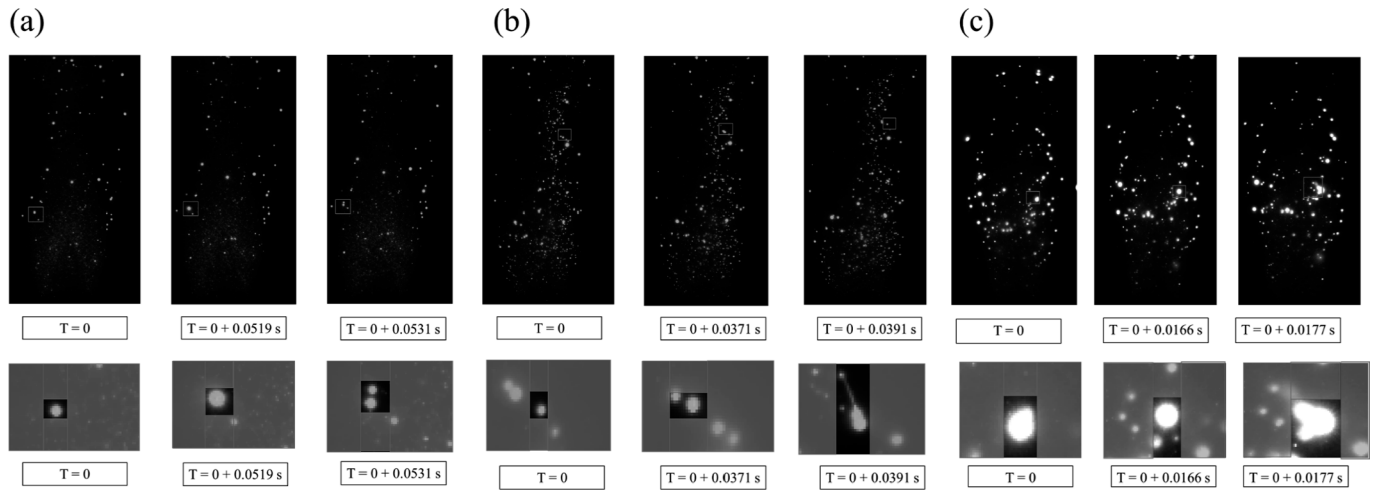


Fig. 7. Iron particle micro-explosion and particle track for (a) iron 2–10 μm case, (b) iron 50 μm case, and (c) iron 100 μm case.

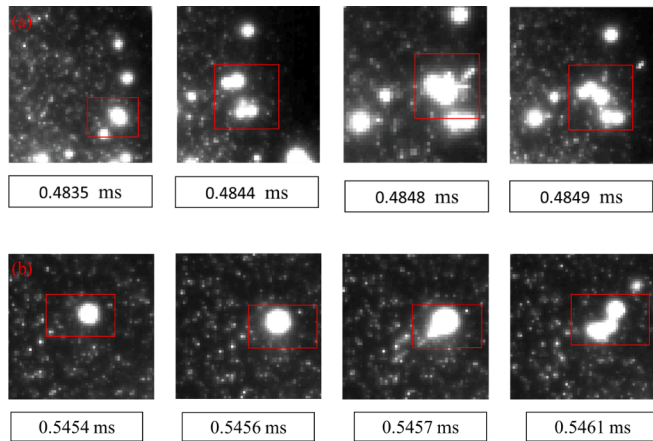


Fig. 8. Micro-explosion particle flying trajectory of iron 2–10 μm with the addition of (a) 5% CO and (b) 10% CO in fuels.

Table 1

(a) Numbers of micro-explosions and micro-explosion probability exhibited by iron particles of different sizes, and (b) micro-explosion probability of iron 2–10 μm with difference CO additions.

Particles size	Micro-explosion in 0.65 s (18,000 fps)
2–10 μm	4 times (–)
50 μm	6 times (20%)
100 μm	24 times (500%)
150 μm	no micro-explosion observed
CO addition	Micro-explosion in 0.65 s (18,000 fps)
0%	4 times (0%)
1%	5 times (25%)
5%	6 times (50%)
10%	9 times (125%)

lower micro-explosion probability than iron particles larger than 50 μm because iron particles smaller than 50 μm are prone to burn in a hybrid flame. However, no micro-explosions were observed when the particle size was 150 μm . Presumably, the 150- μm particles have large momentums in comparison with other small-sized iron particles, and they are prone to fly through methane – air premixed flames with a short residence time. Moreover, the 150- μm iron particles have large bulk volumes and do not easily increase the bulk temperature of iron particles. As a result, a large-sized iron particle could not burn completely within premixed flames, leading to no inception of iron particle micro-

explosion.

Table 1 (b) presents the number of micro-explosions exhibited by 2–10- μm iron particles in hybrid flames under various CO additions. Within a fixed observation period of 0.65 s, the aforementioned particles exhibited four, five, six, and nine micro-explosions under the addition of no CO, 1% CO, 5% CO, and 10% CO, respectively. Thus, the micro-explosion probability of the aforementioned particles was 25%, 50%, and 125% higher under 1%, 5%, and 10% CO addition, respectively, than under no CO addition. The aforementioned results indicated that CO plays a critical role in increasing the micro-explosion probability of iron particles smaller than 50 μm .

3.5. Iron oxide hybrid flames

To determine whether CO addition is the only factor contributing to iron particle micro-explosion, two types of iron oxide particle, namely Fe_3O_4 and Fe_2O_3 , were introduced to the methane–air premixed flames. This process was also conducted to identify intermediate species that could trigger iron particle explosion. The phase diagram of iron particles indicates that before forming the stable oxide Fe_2O_3 , iron particles may exist in the form FeO or Fe_3O_4 as intermediate species. Because FeO is flammable, we hypothesize that it can trigger the iron blinking flame. Here, blinking flames feature an abrupt brightness jump near the end of particle combustion [11]. Thus, compared with iron particles, Fe_3O_4 is more flammable and emits more heat to produce a coupled flame with higher intensity. The images in Fig. 9 indicated that iron oxide particles did not generate micro-explosions when passing through the flame front. In general, Fe_3O_4 consists of Fe_2O_3 and FeO . However, FeO is flammable, and it can trigger the iron blinking flame. Fig. 9a illustrates the flame structure of Fe_3O_4 particles and indicates that Fe_3O_4 has a coupled flame front that is brighter than that of iron particles. Thus, compared with iron particles, Fe_3O_4 is more flammable and emits more heat to produce a coupled flame with higher intensity. The images indicate that iron oxide particles did not generate micro-explosions when passing through the flame front. After burning, Fe_3O_4 transformed into Fe_2O_3 , which is the most stable iron oxide. The flame structure of Fe_2O_3 is shown in Fig. 9b. The images indicate that iron oxide particles did not produce a micro-explosion as they passed through the flame front. Consequently, after iron combustion, Fe_2O_3 is the most stable iron oxide and does not react with an oxidizer, which results in it being unable to produce other oxides.

After burning, Fe_3O_4 transformed into Fe_2O_3 , the most stable iron oxide. The result indicated that Fe_2O_3 particles did not yield a micro-explosion as they passed through the flame front. Consequently, after iron combustion, Fe_2O_3 is the most stable iron oxide and does not react

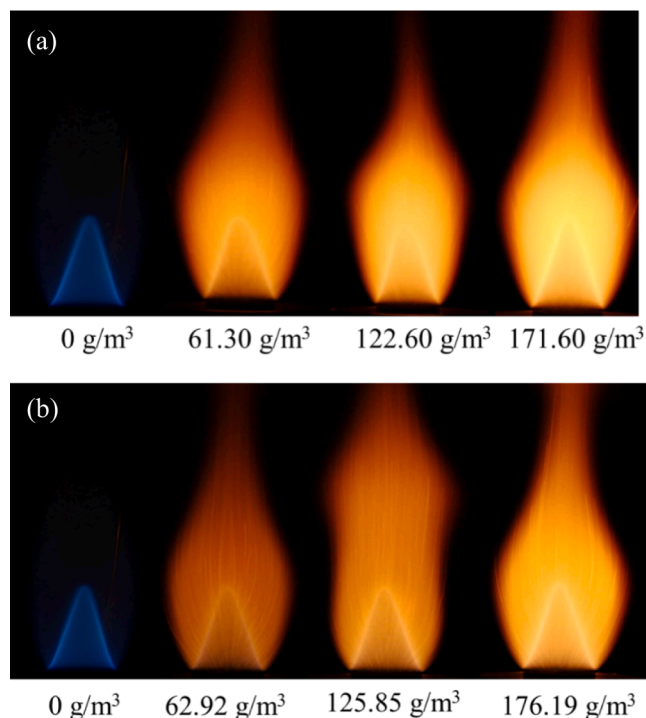


Fig. 9. Flame structure images of (a) Fe_3O_4 and (b) Fe_2O_3 in methane–air premixed flames.

with an oxidizer, which results in it being unable to produce other oxides.

Some studies examined the effect of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) as a flame inhibitor. According to their studies [24–27], $\text{Fe}(\text{CO})_5$ would pyrolyze Fe and CO. The review of Rahinov *et al.* provides a comprehensive insight into the mechanism of combustion synthesis of iron oxide nanoparticles based on combined laser spectroscopy, mass spectrometry, and detailed simulation. In addition, Wen *et al.* [28] examined the thermal decomposition of $\text{Fe}(\text{CO})_5$, pointing out that high-temperature $\text{Fe}(\text{CO})_5$ will be rapidly decomposed into Fe and CO. In general, Fe is prone to react with O_2 to form Fe_3O_4 and Fe_2O_3 . These two particles are stable oxides. However, the redox reaction of Fe_2O_3 or Fe_3O_4 requires CO to convert back to Fe. In this study, 20% and 30% CO was superseded and fueled in the pure methane – air flame. According to the videos taken by the high-speed camera, the addition of CO in iron-oxides – CH_4 –air hybrid premixed flames would trigger the particle micro-explosion, as seen in the **supplementary materials** (file names: “ $\text{Fe}_2\text{O}_3 + 30\%\text{CO}$ ” for the case of Fe_2O_3 with $70\%\text{CH}_4 + 30\%\text{CO}/\text{air}$, “ $\text{Fe}_3\text{O}_4 + 30\%\text{CO}$ ” for the case of Fe_3O_4 with $70\%\text{CH}_4 + 30\%\text{CO}/\text{air}$). It appears that the probability of particle micro-explosion for Fe_2O_3 or Fe_3O_4 is monotonously proportional to the concentration of CO addition in hybrid flames. It conjectures that the resulting iron returning from iron oxides stimulate the formation of $\text{Fe}(\text{CO})_5$ and FeO, bringing into the probability of particle micro-explosion and iron blinking flame occurrence.

3.6. Particle Micro-explosion model

The JANAF thermochemical table [29] indicates that only oxygen reacts with iron in the air. Fig. 10 shows the variation in the Gibbs free energies of formation for iron oxides and carbon oxides with different temperatures. The formation lines of $\text{FeO}(\text{s})$ in the temperature range 1000–1200 K indicate a narrow formation region with Gibbs free energy ranging from –194.316 to –217.819 kJ/mol (a spontaneous reaction). In the aforementioned temperature range, iron particles are oxidized and expanded. Moreover, CO diffuses inside the iron particle’s shell and

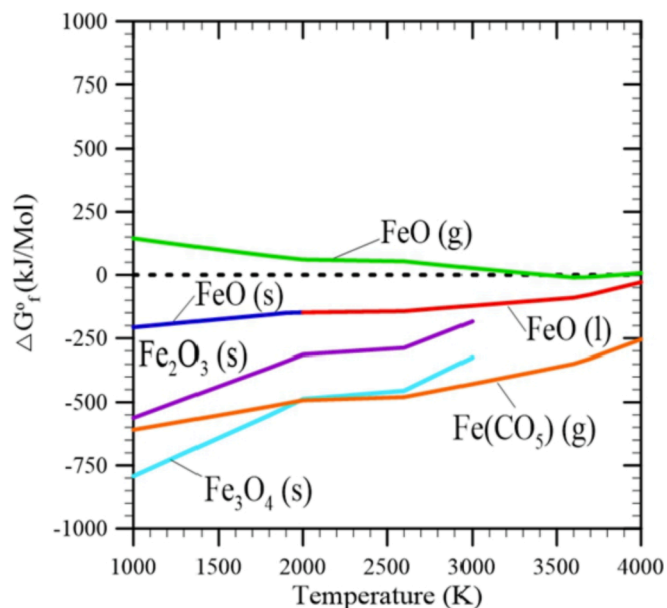


Fig. 10. JANAF Thermochemical for iron and iron oxide particles.

causes the heterogeneous formation of $\text{Fe}(\text{CO})_5$ across the inner surface of the shell. The thermal expansion of iron particles, the severe combustion of trapped CO, and the produced $\text{Fe}(\text{CO})_5$ result in the micro-explosion of these particles. Fe_3O_4 and Fe_2O_3 are formed in the temperature range 1000–3000 K within Gibbs free energy ranges of –250 to –525 and –475 to –725 kJ/mol, respectively.

Regarding the mechanism of the micro-explosion of iron particles, the oxidizer diffuses into iron particles and produces iron oxide in a thin shell. However, limited oxygen heterogeneously reacts over the surface of the iron particles and produces Fe_3O_4 . Fe_3O_4 comprises FeO and Fe_2O_3 . Fe_2O_3 is a stable and rigid oxide; however, when the resulting CO from the methane – air combustion reacts with Fe_3O_4 , this reaction makes Fe_3O_4 redox into fresh Fe particles, and when the Fe predominantly reacts with O_2 , it will lead to FeO. The presence of FeO leads to iron particles blinking and burning after passing through the flame front.

The resulting CO might chemically bind with iron and yield $\text{Fe}(\text{CO})_5$ on the iron surface. Owing to the increasing bulk temperature of the particle, the shell of the particle would form a melting film. In the meantime, the chemically-bonded $\text{Fe}(\text{CO})_5$ might release and form bubbles in the melting film. However, fractional $\text{Fe}(\text{CO})_5$ could further pyrolyze into Fe and CO, resulting in the formation of $\text{Fe}(\text{CO})_5$ and CO mixture bubbles. Alternatively, the melting shell would absorb the surrounding gases and form gaseous bubbles, likening CO, N_2 , and O_2 mixture bubbles. During the agglomeration of the bubbles, the iron particles expand gradually and eventually become hollow spherical particles. However, under special conditions, this condition will induce the micro-explosion of the iron particles. The temperature of $\text{Fe}(\text{CO})_5$ pyrolysis is quite low, but the probability of remaining $\text{Fe}(\text{CO})_5$ bubbles participating in particle micro-explosion could not be negligible. Fig. 11 illustrates the three pathways of iron combustion in methane – air premixed flames: flame blinking, particle expansion, or particle micro-explosion.

4. Conclusions

This present study is to investigate the effect of particle size on iron– CH_4 –air hybrid premixed flames. The result showed that particle size and particle feeding rates were essential to forming a coupled flame front of iron– CH_4 –air hybrid premixed flames. When the feeding rate was increasing, the flame becomes brighter and more stable. Nonetheless, when the particle size increased, the iron heat release is not

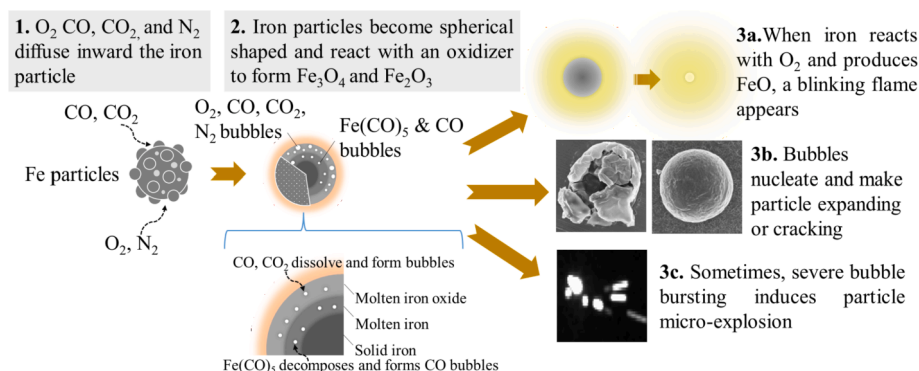


Fig. 11. Iron particles micro-explosion mechanism.

sufficient to make a flame front, but micro-explosions occurred during the iron-CH₄-air hybrid premixed flames. Regarding the mechanism of the micro-explosion of iron particles, the oxidizer diffuses into iron particles and produces iron oxide in a thin shell. However, limited oxygen heterogeneously reacts over the surface of the iron particles and produces Fe₃O₄. Fe₃O₄ comprises FeO and Fe₂O₃. Fe₂O₃ is a stable and rigid oxide; however, when CO reacts with Fe₃O₄, this reaction makes Fe₃O₄ redox into fresh Fe particles. Sequentially, the resulting Fe reacts with O₂ and produces FeO. The presence of FeO leads to iron particles blinking and shrinking right away after passing through the flame front. The surrounding CO might chemically bind with iron and yield Fe(CO)₅ on the iron surface. Depending upon the increase of bulk temperature of iron particles, partial Fe(CO)₅ could further pyrolyze into Fe and CO, resulting in the formation of Fe(CO)₅ and CO mixture bubbles. In the meantime, the melting shell would absorb the surrounding gases and form CO, N₂, and O₂ mixture bubbles. During the agglomeration of the bubbles, the iron particles expand gradually and eventually become hollow spherical particles. However, under special conditions, this condition will induce the micro-explosion of the iron particles.

CRediT authorship contribution statement

Yueh-Heng Li: Conceptualization, Funding acquisition, Supervision, Project administration, Writing – review & editing. **Aris Purwanto:** Data curation, Formal analysis, Methodology, Writing – original draft. **Bo-Cheng Chuang:** Data curation, Formal analysis, Writing – original draft.

Declaration of Competing Interest

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

Acknowledgment

Financial support for this work was provided by the Ministry of Science and Technology (Taiwan) under grant numbers MOST 108-2628-E-006-008-MY3 and MOST 109-2221-E-006-037-MY3.

References

- [1] Berghthorson JM, Goroshin S, Soo MJ, Julien P, Palecka J, Frost DL, et al. Direct combustion of recyclable metal fuels for zero-carbon heat and power. *Appl Energy* 2015;160:368–82.
- [2] Julien P, Whiteley S, Goroshin S, Soo MJ, Frost DL, Berghthorson JM. Flame structure and particle-combustion regimes in premixed methane-iron-air suspensions. *Proc Combust Inst* 2015;35(2):2431–8.
- [3] Tang F-D, Goroshin S, Higgins AJ. Modes of particle combustion in iron dust flames. *Proc Combust Inst* 2011/01/01/ 2011.;33(2):1975–82.
- [4] Tang F-D, Goroshin S, Higgins A, Lee J. Flame propagation and quenching in iron dust clouds. *Proc Combust Inst* 2009/01/01/ 2009.;32(2):1905–12.
- [5] Bidabadi M, Mafi M. Time variation of combustion temperature and burning time of a single iron particle. *Int J Therm Sci* 2013/03/01/ 2013.;65:136–47.
- [6] McRae M, Julien P, Salvo S, Goroshin S, Frost DL, Berghthorson JM. Stabilized, flat iron flames on a hot counterflow burner. *Proc Combust Inst* 2019;37(3):3185–91.
- [7] Poletaev NI, Khlebnikova MY. Combustion of Iron Particles Suspension in Laminar Premixed and Diffusion Flames. *Combust Sci Technol* 2022;194(7):1356–77.
- [8] Li YH, Pangestu S, Purwanto A, Chen CT. Synergetic combustion behavior of aluminum and coal addition in hybrid iron-methane-air premixed flame. *Combust Flame* 2021;228:364–74.
- [9] Huang J, et al. A detailed study on the micro-explosion of burning iron particles in hot oxidizing environments. *Combust Flame* 2021/09/28/ 2021.;111755.
- [10] Ning D, Shoshin Y, van Oijen JA, Finotello G, de Goey LPH. Burn time and combustion regime of laser-ignited single iron particle. *Combust Flame* 2021/08/01/ 2021.;230:111424.
- [11] Ning D, Shoshin Y, van Stiphout M, van Oijen J, Finotello G, de Goey P. Temperature and phase transitions of laser-ignited single iron particle. *Combust Flame* 2022/02/01/ 2022.;236:111801.
- [12] Yu J, Zhang X, Zhang Qi, Wang L, Ji Ke, Peng L, et al. Combustion behaviors and flame microstructures of micro- and nano-titanium dust explosions. *Fuel* 2016;181:785–92.
- [13] Badiola C, Dreizin EL. Combustion of micron-sized particles of titanium and zirconium. *Proc Combust Inst* 2013;34(2):2237–43.
- [14] Wainwright ER, Lakshman SV, Leong AFT, Kinsey AH, Gibbins JD, Arlington SQ, et al. Viewing internal bubbling and microexplosions in combusting metal particles via x-ray phase contrast imaging. *Combust Flame* 2019;199:194–203.
- [15] Wainwright ER, Schmauss TA, Vummidi Lakshman S, Overdeep KR, Weihs TP. Observations during Al: Zr composite particle combustion in varied gas environments. *Combust Flame* 2018;196:487–99.
- [16] Chen G-B, Li Y-H, Lan C-H, Lin H-T, Chao Y-C. Micro-explosion and burning characteristics of a single droplet of pyrolytic oil from castor seeds. *Appl Therm Eng* 2017;114:1053–63.
- [17] Tarlet D, Bellettre J, Tazerout M, Rahmouni C. Prediction of micro-explosion delay of emulsified fuel droplets. *Int J Therm Sci* 2009/02/01/ 2009.;48(2):449–60.
- [18] Aly Y, Schoenitz M, Dreizin EL. Ignition and combustion of mechanically alloyed Al–Mg powders with customized particle sizes. *Combust Flame* 2013;160(4):835–42.
- [19] Garra P, Leyssens G, Allgaier O, Schönnenbeck C, Tschamber V, Brillhac J-F, et al. Magnesium/air combustion at pilot scale and subsequent PM and NO_x emissions. *Appl Energy* 2017;189:578–87.
- [20] Liu X, Schoenitz M, Dreizin EL. Preparation, ignition, and combustion of magnesium-calcium iodate reactive nano-composite powders. *Chem Eng J* 2019;359:955–62.
- [21] Chintersingh K-L, Sun Y, Schoenitz M, Dreizin EL. Heterogeneous reaction kinetics for oxidation and combustion of boron. *Thermochim Acta* 2019;682:178415.
- [22] Lysenko EN, Surzhikov AP, Zhuravkov SP, Vlasov VA, Pustovalov AV, Yavorovsky NA. The oxidation kinetics study of ultrafine iron powders by thermogravimetric analysis. *J Therm Anal Calorim* 2013;115(2):1447–52.
- [23] Corcoran A, Mercati S, Nie H, Milani M, Montorsi L, Dreizin EL. Combustion of fine aluminum and magnesium powders in water. *Combust Flame* 2013;160(10):2242–50.
- [24] Nanjiah M, et al. Experimental and numerical investigation of iron-doped flames: FeO formation and impact on flame temperature. *Proc Combust Inst* 2021;38(1):1249–57.
- [25] Wlokas I, Faccinnetto A, Tribalet B, Schulz C, Kempf A. Mechanism of Iron Oxide Formation from Iron Pentacarbonyl-Doped Low-Pressure Hydrogen/Oxygen Flames. *Int J Chem Kinet* 2013;45(8):487–98.
- [26] Rumminger MD, Reinelt D, Babushok V, Linteris GT. Numerical study of the inhibition of premixed and diffusion flames by iron pentacarbonyl. Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States. *Combust Flame* 1999/01/01/ 1999.;116(1):207–19.
- [27] Rahinov I, Sellmann J, Lalanne MR, Nanjiah M, Dreier T, Cheskis S, et al. Insights into the Mechanism of Combustion Synthesis of Iron Oxide Nanoparticles Gained by Laser Diagnostics, Mass Spectrometry, and Numerical Simulations: A Mini-Review. *Energy Fuels* 2021;35(1):137–60.

- [28] Wen JZ, Goldsmith CF, Ashcraft RW, Green WH. Detailed Kinetic Modeling of Iron Nanoparticle Synthesis from the Decomposition of $\text{Fe}(\text{CO})_5$. *The Journal of Physical Chemistry C* 2007/04/19 2007.;111(15):5677–88.
- [29] Malcolm W. Chase, Jr., *NIST-JANAF thermochemical tables*. Fourth edition. Washington, DC : American Chemical Society ; New York : American Institute of Physics for the National Institute of Standards and Technology, 1998., 1998.
- [30] Huang Chao-Wei, Li Yueh-Heng, Xiao Kai-Lin, Lasek Janusz. Cofiring characteristics of coal blended with torrefied Miscanthus biochar optimized with three Taguchi indexes. *Energy* 2019;172:566–79. <https://doi.org/10.1016/j.energy.2019.01.168>.
- [31] Li Yueh-Heng, Lin Hsien-Tsung, Xiao Kai-Lin, Lasek Jnusz. Combustion behavior of coal pellets blended with Miscanthus biochar. *Energy* 2018;163:180–90. <https://doi.org/10.1016/j.energy.2018.08.117>.